REACTIONS OF UREA PHOSPHATE IN CALCAREOUS AND ALKALINE SOILS: AMMONIA VOLATILIZATION AND EFFECTS ON SOIL SODIUM AND SALINITY

by

Abdul-Mehdi Saleh Ali

A Dissertation Submitted to the Faculty of the

DEPARTMENT OF SOIL AND WATER SCIENCE

In Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

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Reactions of urea phosphate in calcareous and alkaline soils: Ammonia volatilization and effects on soil sodium and salinity

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The University of Arizona, 1989

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As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Abdul-Mehdi Saleh Ali

entitled Reactions of Urea Phosphate in Calcareous and Alkaline Soils: Ammonia Volatilization and Effects on Soil Sodium and Salinity

and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

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I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

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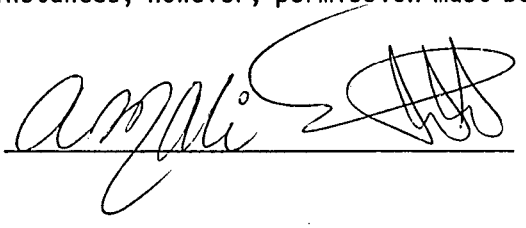
SIGNED: 

DEDICATION

To my deceased parents, my son Assad, and my daughters, Ghydaa and Raida.

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ABSTRACT

Nitrogen (N) loss in the form of volatilized ammonia (NH_3) is a considerable problem when ammonium (NH_4^+) forming fertilizers are applied to calcareous or alkaline soils. Large areas of agricultural land, contain alkalinity and salinity problems, are potentially suitable for crop production with little alteration. This study was conducted to determine and compare the effectiveness of urea phosphate (UP) in reducing soil alkalinity and NH_3 loss.

The volatilization of NH_3 from UP and urea (U) was studied on 3 selected soils (Hayhook SL, Laveen L and Latene L) using an aeration system. Urea phosphate and U were each applied at rates of 0, 50, 100 and 200 ppm-N either to the surface dry or in solution or mixed with the soil. The volatilized NH_3 was trapped in sulfuric acid. sampled periodically and analyzed for N using the semi microkjeldahl distillation apparatus.

The effect of UP, Sulfur-Foam (SF), Phosphuric Solution (PHP) and a mixture of SF and UP (Mix) on leaching soil sodium (Na) and salinity was also studies on two soils (Pima L and Crot CL) in columns. Each of these amendments was applied at a rate of one and two equivalent amounts of the exchangeable Na_{ex}.

The highest N loss in the form of NH_3 occurred when U was applied to Hayhook soil. However, UP applied to Hayhook soil (neutral to acidic, coarse textured and low $CaCO_3$ content) resulted in the lowest NH_3-N loss. Less NH_3-N loss was found from U application to Laveen and Latene soils (fine textured with higher $CaCO_3$ content) than with Hayhook soil. The

general trend was higher N loss, in the form of volatilized NH_3, with surface application dry or in solution than when mixed with the soil. This trend showed an increase in the amount of volatilized NH_3 with increasing rate of N application.

Urea phosphate was as effective as PHP or Mix (acid containing fertilizers) treatments in reducing soil salinity and alkalinity in Pima and Crot soils. No difference was found between rates of application (1 and 2 equivalent amount of Na_{ex}) except for soil pH. A similar trend in the decrease in soil salinity was found to that of the pH which was in the order PHP, UP, Mix, SF and control treatments. No significant difference was found between SF and control treatments in all parameters. No significant difference was found between treatments for exchangeable Ca. This was affected by the Ca compounds present in the soil.

Generally, UP is a potential fertilizer for supplying N and phosphorus (P) as plant nutrients, reducing NH_3 volatilization, and can be used as a soil amendment to control soil salinity and alkalinity.

CHAPTER 1

INTRODUCTION

Agricultural and industrial development go hand in hand. Agricultural improvement contributes to general economic development in several ways. Many of the physical inputs such as fertilizers or soil amendments are supplied by industries. An actual need to support the rapidly growing population of today's world could be met by substantial increases in agricultural production (Olson et al., 1971). Bringing more land under cultivation is a step in increasing agricultural production, but large areas of virgin land have alkalinity and salinity problems. Therefore, economical and practical reclamation practices will be required for any large scale expansion.

It is obvious that larger tonnages of plant nutrients will be increasingly removed under intensive agricultural production and agricultural land in unlimited quantities no longer available. Therefore, the development of a potential nutrient-demand base will be necessary to maintain soil fertility levels and crop production. The development of a sound fertilizer industry has contributed to the overall economics of agricultural production.

The two fertilizer elements most commonly supplied by farmers under irrigated conditions are nitrogen and phosphorus. Losses of ammonia (NH_3), from applied fertilizer nitrogen, are a concern to everyone involved with using nitrogen fertilizer. A product which has been developed and is currently being produced and evaluated by the Tennessee Valley

Authority shows promise of having properties which are suitable for solving problems of irrigated alkaline soils. Characteristics of the product urea phosphate (UP) are: (a) readily dissolves in irrigation water, (b) is initially acidic, (c) initially free of ammoniacal nitrogen and (d) contains phosphorus in the form of phosphoric acid.

In this study two experiments were carried out to investigate the reactions of UP in alkaline soils. The objectives of this study were to:

1. Measure NH_3 losses from soils treated with various rates and methods of application of UP.

2. Determine the efficiency and effective rate of UP that will aid leaching the Na^+ and salts from alkaline soils.

CHAPTER 2

LITERATURE REVIEW

Acid Fertilizers

An understanding of the initial and long-term reaction of fertilizers with soil is required for the intelligent use of fertilizers. This is important for acid or acid-forming fertilizers. Depending on the nature of the soil as well as the method and application rate, the reaction of acid fertilizers will vary when they are applied to soils (Jones, 1984). Acid addition to fluid formulations is a recent development in fertilizer materials, that causes soils to become more acidic with time. The exception of the acidic fluid fertilizers is materials with free ammonia such as anhydrous ammonia, aqua ammonia or ammonium polysulfide (Luckhardt, 1984). Reacting urea with nitric acid [$CO(NH_2)_2 \cdot HNO_3$], sulfuric acid [$CO(NH_2)_2 \cdot H_2SO_4$] or phosphoric acid [$CO(NH_2)_2 \cdot H_3PO_4$] will usually form acid fertilizers that have a pH of 1 to 3. Based on work by TVA in 1980, crystalline or granular urea phosphate of pH 1 to 3 was produced which has the characteristics of an acid. As a nitrogen source, the urea phosphate is equivalent to urea under most conditions or superior under conditions when ammonia volatilization can occur and in enhancement of micronutrient availability (Achorn, 1984).

Gregory (1984) reported interesting properties of the urea-sulfuric acid fertilizer such as:

"- a nitrogen fertilizer with up to 28% N,
- a sulfur fertilizer with up to 18% S,
- a remedy for excess bicarbonate in irrigation water,
- a product for reclaiming sodic soils, comparable in effect to sulfuric acid but safer to handle and use."

This fertilizer can be applied to the soil by broadcasting or side-dressing or in the irrigation water or injecting it in drip systems. Aasum (1981) reported that nitrophosphate fertilizer technology becomes an increasingly attractive alternative to sulfuric acid-base fertilizer production methods as the cost of sulfur increases.

Ammonia Volatilization

Economic and environmental considerations have stimulated interest in the exchange of gaseous N compounds between the atmosphere and soil, plant and water surfaces (Harper, et al., 1983). Appreciable amounts of NH_3 can be volatilized when ammoniacal fertilizers are applied to calcareous soils. Effective use of urea on crops requiring surface fertilizer applications is limited by high ammonia loss (Fenn, Taylor and Matocha, 1981).

Many investigators have studied directly or indirectly the effects of pH on NH_3 volatilization. The general conclusion is that the higher the pH, the greater the NH_3 loss (Bremner and Douglas, 1971; Fenn and Kissel, 1973; Velk and Stumpe, 1978; Stroehlein, Yahia and Pennington, 1980; Maktari, 1983; Mashhady, 1983; and Ferguson et al., 1984). Other factors which influence NH_3 volatilization from soil such as cation exchange capacity, exchangeable cations, texture, temperature, water

content and the species of ammonium salt have also been studied by many investigators.

The nature of reactions of the chemicals with water and soil will cause additional problems with water-applied ammonia. Low salt waters or water containing high quantities of Na^{+} than Ca^{2+} cause problems in relation to the application of NH_3 to different water quality. Increasing the alkalinity reduces NH_3 solubility and leads to high NH_3 loss, whereas lowering the pH reduces Ca^{2+} precipitation and NH_3 loss (Stroehlein et al., 1980; Miyamoto and Ryan, 1976). In a lab study approximately 50% of the applied NH_3 was lost within 12 hours from still water at NH_3 application rates greater than 100 mg of NH_3/liter and approximately 70% was lost within 24 hours from still water and within 12 hours from the rotated water. Ammonia loss was influenced by the differences in irrigation water quality which changes the degree of dissociation of NH_4OH (Miyamoto, Ryan and Stroehlein, 1975). If anhydrous NH_3 is applied in irrigation water, the length of irrigation run should be shortened, especially in light-textured soils. Acid treatments in irrigation water reduced the carbonate and bicarbonate concentrations and reduced NH_3 volatilization by increasing nitrate-nitrogen (Yahia and Stroehlein, 1980). Using KN_3 and N-serve as nitrogen inhibitors, Cochran, Papendick and Woody (1973) reported that during the first 8 weeks after injection, in non-irrigated treatment, the NH_4^{+}-N concentration for NH_3 alone decreased whereas NO_3^{-}-N accumulated rapidly. The concentrations of both NH_4^{+} and NO_3^{-} remained relatively stable after 8 weeks. Ammonium-N (NH_4^{+}-N concentrations decreased rapidly

with the first irrigation with KN_3, whereas it did not decline noticeably with N-serve until at least 8 weeks after fertilization.

Maktari (1983) reported that salts, moisture and their interactions significantly affected NH_3 volatilization in Laveen and Gila soils. Ammonia loss from native soil nitrogen was significantly increased by salts, whereas moisture effect was significant on Laveen soil and their interaction in both soils was not significant. In both soils, increasing the salt concentration (NaCl) and lowering the moisture content increased nitrogen losses as NH_3. Connell, Meyer, and Cstlson (1979) also studied the moisture effect on NH_3 loss. They found that when Dinuba sandy loam soil was treated with urea and held at field capacity, losses approached 8% of the applied nitrogen with low relative humidity air flowing over the soil surface, whereas intermediate losses of nitrogen resulted with a high relative humidity air. Most of the loss occurred within 10 days following urea application.

Many investigators studied the effect of nitrogen source, rate and method of application on NH_3 volatilization. The general conclusion is that NH_3 losses were greater from NH_4^+ containing compounds and urea than other N compounds. (Maktari, 1983; Bremner and Douglas, 1971; Morel, Varade and Bharambe, 1977; Vlek and Stumpe, 1978; Fenn and Kissel, 1973; Stumpe, Vlek and Lindsay, 1984; Mashhady, 1983; and Torello,Wehner and Turgeon, 1983). Also greater loss can be anticipated with increased application rate (Connell et al., 1979; Vlek and Stumpe, 1978; and Stumpe et al., 1984). Greater nitrogen losses should also be expected when the

fertilizers were applied to the surface than when incorporated (Mashhady, 1983; Fillery, Simpson and DeData, 1984; Torello ete al. 1983).

A linear relationship was found between the amount of urea-N hydrolyzed and incubation time. The decrease in urea hydrolysis rate by soil urease was in the order: urea > urea oxalate > urea nitrate > urea phosphate. A significant reduction in urease activity in Fayette and Webster soils was found by addition of 100 ppm (soil basis) of N+ as H_3PO_4. A loss of 21.2% of the urea-N as NH_3 resulted after 14 days of treating the soil with urea, whereas only 0.7% was lost for the soils treated with urea phosphate (Bremner and Douglas, 1971). Avnimelich and Laher (1977) discussed the possibility of measurements of NH_3 in the air directly or indirectly in solution equilibrated with the atmosphere. Only when the buffer capacity of the soil is high or with low NH_4^+ concentration in soil solution, the pH becomes of prime importance. Reduced NH_3 losses result from adsorption of NH_4^+ which leads to a decrease in NH_4^+ ion and NH_3 concentration in soil solution. The effect of solution chemistry and environmental conditions on NH_3 volatilization was also studied by Vlek and Stumpe (1978). They indicated that NH_3 loss rate from aqueous systems is a function of the partial pressure difference of NH_3 in air and water with adequate mixing. An increase in NH_3 loss can be expected with the presence of $CaCO_3$ or any other suitable buffer in the underlying soil, therefore, in the case of urea, all NH_4^+ in solution can be lost before the solution becomes acidic and NH_3 loss ceases. A linear increase in evaporation losses with increasing airflow and also water turbulence tends to increase

NH_3 loss due to the enhanced replenishment of the air-water NH_3 interface. Increasing the temperature increases the hydrolysis constant of NH_3.

Fenn et al. (1981) studied the significance of soluble Ca^{2+} and Mg^{2+} in controlling NH_3 loss from surface-applied N fertilizer. They reported that a great improvement in N retention should result if CO_3 reacts with Ca^{2+} and Mg^{2+} on the soil surface. Their results indicated maximum NH_3-N loss from urea applied alone, whereas Ca^{2+} and Mg^{2+} reduce the effects on NH_3 loss from urea. $CaCl_2$ and $Ca(NO_3)_2$ were more effective in reducing NH_3 loss than $CaSO_4$, however, no differences were found between $CaCl_2$ and $Ca(NO_3)_2$. $CaSO_4$ resulted in NH_3 loss not less than that found with urea alone. $CaCl_2$ and $Ca(NO_3)_2$ reduced soil pH, whereas, because of the low solubility of $CaSO_4$, no reduction in soil pH occurred. Reduced NH_3 loss resulted from the precipitation of CO_3 as $CaCO_3$ at pH values of 7.0 or from decomposition of H_2CO_3 in acid soils. A weakly acidic product such as NH_4Cl or NH_4NO_3 will form upon the removal of CO_3. Kissel, Brewer and Arkon (1977) designed a system to measure NH_3 loss under field conditions from N fertilizers. The basic components of the system are "a vacuum pump, a chemical trap to capture NH_3, and the volatilization chamber." Continuously measuring NH_3 volatilization in the field with a minimum disturbance of the actual field environment was the main advantage of the system. Fenn and Kissel (1973) proposed a mechanism for NH_3 volatilization from calcareous soils. They suggested that NH_4^+ compounds will react with the solid state $CaCO_3$ when applied to the surface of a calcareous soil forming $(NH_4)_2CO_3$. The general reaction is:

$$"X(NH_4)_z\ Y + N\ CaCO_3\ (S) \rightleftharpoons N(NH_4)_2CO_3 + Ca_nY_x$$

$$(NH_4)_2CO_3 + H_2O \rightleftharpoons 2NH_3 \uparrow + H_2O + CO_2 \uparrow$$

$$\uparrow \downarrow$$

$$2NH_4OH$$

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH \rightleftharpoons NH_3 \uparrow + H_2O$$

where Y is the anion of the NH_4 salt with N, X and n are values which depend on the anion and cation valences."

The amounts of NH_4OH that will be formed depends on Ca_nY_x solubility and its rate of formation. In their experiments using different sources of NH_4^+[$(NH_4)_2$-SO_4, NH_4F, $(NH_4)_2HPO_4$, NH_4NO_3, NH_4Cl, and NH_4I], they reported that during the first hours the initial loss of NH_3-N was greatest from NH_4F, intermediate from $(NH_4)_2SO_4$ and $(NH_4)_2HPO_4$ and lowest from NH_4NO_3, NH_4Cl and NH_4I. Harper et al. (1983) reported that the atmospheric NH_3 concentration close to the ground decreases with increasing height when the net transport of NH_3 is out of the soil-plant system and into the atmosphere and vice versa. They also reported three distinct flux density patterns after urea application. In the summer and spring, an increase in the NH_3 efflux began within 10 hours and reached maximum values within 24 hours, then declined to near background concentrations after 4 days. In autumn NH_3 loss began 8 hours after application with large flux densities during the day time for the next 5 to 7 days. In winter, continuous moderate flux densities for 6 to 8 days began within 24 hours.

Ammonia efflux increased to high rate when urea was applied to wet soil, whereas a slow or moderate NH_3 efflux was found when urea was applied to dry soil. Also diurnal fluctuations with the highest outward NH_3 fluxes occurring during periods of highest solar radiation were apparent.

Incubation of calcareous soils at high temperature is more conducive to NH_3 loss, which is irrespective of the N source. The rate of nitrification was less at low temperature than that at higher temperature. High N losses were associated with soils low in cation exchange capacity (CEC) (Mashhady, 1983). Soil organic matter and soil type greatly influence losses of applied NH_4^+-N. Soils that are silty clay loam, high in CEC and high in organic matter content, decreased NH_4^+-N loss because of adsorption of NH_4^+-N on soil cation exchange complex and immobilization into the organic fraction. Also the decreased diffusion of the applied NH_4^+-N from the anaerobic soil layer to the surface aerobic soil layer, due to the high NH_4^+-N adsorption, resulted in a decreased N loss. A similar trend to those of NH_4^+-N was found with urea-N losses (Reddy and Patrick, 1980). Ammonia volatilization follows a characteristic diurnal pattern in which the NH_3 loss peak was at midday and was lowest overnight. This could be attributed to temperature and wind speed changes. Ammonia loss increased linearly with both partial pressure of NH_3 and wind speed (Fillery et al., 1984) Stumpe et al. (1984) reported that the cumulative percentage volatilization losses from Uvalde soil of the applied ^{15}N volatilized as NH_3 was not affected by the application rate of urea. Doubling the application rate of urea doubled the absolute quantity of ^{15}N volatilized. They also found a significant decrease in the quantity of

volatilized NH_3 in the first week of the experiment as the initial moisture content decreased. The decrease in NH_3 loss was due to delayed dissolution and hydrolysis of urea in soil. Significantly less NH_3 volatilized from urea phosphate than urea. There was an insignificant trend toward decreased NH_3 loss with increasing additions of H_3PO_4 when urea and various urea phosphates were added to Ravola soil. Addition of pyrophosphate was no help in reducing NH_3 loss. In soils with low calcite contents a much greater reduction in NH_3 loss was observed for urea phosphate compared with NH_3 losses from urea. Ferguson et al. (1984) observed that at maximum pH of the soil surface, the hydrolysis of urea was rapid; about 70% of the urea had been hydrolyzed by 2 days and over 90% by 6 days after application. The time required for complete urea hydrolysis closely corresponded to the time when the soil solution pH began to decline, indicating that NH_3 was being volatilized faster than it was being added to the soil solution by hydrolysis. They also reported that soils with higher or more H^+ buffering capacity would allow less of the ammoniacal N to become NH_3 and thus reduce the potential for volatilization.

Using phenyl phosphorodianridate (PPD) as a urease inhibitor, Byrnes, Savant and Crowell (1983) observed that PPD completely prevented losses of top dressed urea, urea hydrolysis inhibition delayed the supplying of NH_4^+-N to nitrifying organisms and reduced NH_3-N concentration, thus reduced NH_3 volatilization. Torello et al. (1983) reported negligible NH_3 losses from turf samples that had been fertilized with S-coated urea -N (SCS) source. Bouwmeester, Vlek and Stumpe (1985) studied the factors that contribute most significantly to NH_3 loss in a simulated

semiarid environment following urea application. They found a significant decrease in the amount of N lost from the soil-plant system with increasing rainfall, irrespective of the initial soil water content. The increased rainfall caused a downward movement of the urea restricting its hydrolysis and dissolution on the surface. Wind generally has a drying effect on the soil which impedes NH_3 loss. Finally, the volatilization of NH_3 from nitrogen containing fertilizers has received attention for many years. The loss mechanism in soils and the factors affecting the magnitude of NH_3 loss has been discussed in numerous studies (Terman, 1979; Faurie and Bardin, 1979, as cited by Bouwmeester et al., 1985).

Soil Sodium and Salinity

One of the most common soil tests in evaluating soil fertility and salinity problems is soil pH measurement. The controlling factor of soil pH in moderately alkaline soils is excess native lime, whereas high Na^+ ion concentrations causes high pH values in strongly alkaline soils. The use of acidifying amendments can reduce soil pH values. Soil pH changes with the use of acidifying amendments such as sulfuric acid, from two reactions. First, is the dissolution of the lime which provides a source of soluble Ca^{2+}. This soluble Ca^{2+} will replace the exchangeable Na^+ which may then be leached away. The second major pH reduction is due to the reaction of the acidifying amendment with almost all of the remaining lime. Thus there will be little change in soil pH until most of the lime is dissolved (Stroehlein, 1980).

The development and maintenance of successful agricultural reclamation projects involves the control of salinity and alkalinity problems. Excess removal of salts with the addition of chemical amendments with adequate irrigation water supply may be required for soils that are initially saline. On the other hand, improper irrigation procedures and soil management practices with inadequate drainage may lead to unproductive soils even if they were initially nonsaline because of the accumulation of excess soluble salts and exchangeable Na^+ (Allison et al., 1954). Prevention of excessive salt accumulation could be accomplished by the removal of salts in amounts about equal to salts applied by irrigation water (salt balance concept). This can be done by applying adequate water to percolate through and leach the root zone. Irrigation water with high Na^+ content will result in a soil high in sodium after several irrigations. Sodium accumulation to concentrations exceeding crop tolerance may result in damage. If Ca^{2+} is present, this damage can be reduced (Ayers and Westcot, 1976). NcNeal and Coleman (1966) stated that a major concern is maintaining sufficiently high soil permeability for salinity control in irrigated agriculture. Hydraulic conductivity and infiltration rate are indices of permeability. These indices are commonly dependent on both the exchangeable sodium percentage (ESP) of soil and salt concentration of the percolating solution. Soil permeability decreases with increasing sodium adsorption ratio (SAR) and decreasing electrical conductivity (ECe) of the solution.

Increasing the electrolyte concentration in a solution, up to 1 M, increases gypsum ($CaSO_4 \cdot 2H_2O$) solubility. Gypsum solubility in different

Na^+ salts of the same concentrations was found to be NaOAC > $NaNO_3$ > NaCl > $NaClO_4$ (Nakayama, 1971). Nakayama (1969) also stated that supplying Ca^{2+} from gypsum compared to other Ca^{2+} sources is restricted by the limited solubility of $CaSO_4$ and the limited solubility of $CaCO_3$ which is also a function of solution pH, decreasing with increasing pH.

Role of Sulfur in Land Reclamation

Sulfur is an essential nutrient element for the members of the plant and animal kingdoms. Sulfur is widespread in soils in both the available and unavailable states. It is commonly used in reclaiming sodic or alkali soils and in controlling certain plant pathogens (Alexander, 1976). Practically all of the sulfur in many soils is organic; with most of it tied up in complex humus molecules with normally low concentrations of uncombined organic sulfur compounds. Inorganic sulfate is formed by the transformation of organic sulfur by heterotrophic microorganisms (Freney and Stevenson, 1966).

Many investigators have studied the effect of sulfur application on soil pH. The general conclusion is that there was a decrease in soil pH with an increase in soil sulfate because of increased hydrogen ion concentra-tion in the soil (Nor and Tabatabai, 1977; Pepper, 1975; Saleh, 1980; Alawi, 1977; Miyamoto, et al., 1975; Attoe and Olson, 1966; Lie and Caldwell, 1966; and Dawood, 1980). Armstrong et al. (1975) found an increase in wheat yield by treating a clay loam soil with 95% commercial grade H_2SO_4 in irrigation water low in soluble salts, but high in Na^+. Yahia (1974), Miyamoto et al. (1975), Alawi (1977) and Stroehlein (1980)

reported that acid application reduced bicarbonate content by dissolving lime ($CaCO_3$) to provide a source of Ca^{2+} for replacement of exchangeable Na^+, which can then be leached away. Also, Yahia (1974) and Alawi (1977) stated that for deeper leaching, H_2SO_4 application reduces the time and amount of water required to leach the soil to a specific EC compared to gypsum. Alawi (1977) also stated that soil in gypsum treated columns required more water than H_2SO_4 treated columns. With H_2SO_4 treatments, more salt can be removed from the soil per unit volume of water than with gypsum or untreated soils. Margolis (1974) reported a decrease in SAR and ESP values associated with acid and acidifying amendment applications which lower the sodium hazard, however, Ca^{2+} and Mg^{2+} concentrations increased in the soil solution as a result of the dissolution of Ca^{2+} compounds. This was accomplished by a decrease in the water soluble and exchangeable Na^+ concentration. Generally acid treated soil gave significantly higher infiltration rates by increasing water penetration into the soil.

Surface applied H_2SO_4 was more effective than chemically equivalent amounts of surface applied gypsum in reclaiming Na^+ saturated soils or soils with adequate $CaCO_3$ (Overstreet, Martin and King, 1951). In noncalcareous soil reclamation, gypsum can be used (Yahia, 1974; Alawi, 1977). Severe Ca^{2+} precipitation takes place under alkaline conditions in irrigation water or soils. Sulfuric acid application neutralizes the alkalinity, reduces Ca^{2+} precipitation and exchangeable Na^+ and consequently prevents a decline in infiltration rate (Miyamoto and Ryan, 1976). In a study of sulfur byproducts, Dawood (1980) found that "foam

sulfur" was more effective than "cake sulfur" and significantly higher than elemental sulfur in releasing salts into the soil solution.

CHAPTER 3

MATERIALS AND METHODS

Soils

Two experiments were conducted in this study utilizing five different soils. These soils were Laveen loam (coarse-loamy, mixed, hyperthermic, Typic Calciorthids) which contains more than 15% $CaCO_3$ equivalent at depths below about 46 cm. This soil was collected from the University of Arizona Farm at Mesa. Hayhook sandy loam (coarse-loamy, mixed, nonacid, thermic, Typic Torriorthents) is deep, well-drained, moderately-rapidly permeable and formed in alluvium. This soil was collected from west of Tucson near Highway 86 northwest of Sandario Road. Latene loam (coarse-loamy, mixed, thermic, Typic Calciorthids) contains 20 to 35% $CaCO_3$ accumulation in the C horizon. This soil was collected near Campbell Avenue and Prince Road area in Tucson, Arizona. Pima loam (fine-silty, mixed, calcareous, thermic, Typic Torrifluvents) soil is calcareous and mildly alkaline to moderately alkaline, was collected from a saline-sodic area on the University of Arizona Safford Agricultural Center. Crot clay (clayey, mixed, thermic, Aquic Natrustalfs) soil is strongly alkali or saline alkali, has distinct horizons of carbonate accumulation, and is somewhat poorly drained. It was collected near State Highway 186, 3 miles southwest of Willcox.

These soils were collected from the surface 0 to 30 cm layer, air dried, ground to pass a 2 mm sieve, mixed thoroughly and stored for subsequent use. The first three soils were used in measuring NH_3

volatilization from the UP and U study. The Pima and Crot soils were used to determine the effects of UP and leaching on soil sodium and salinity. Selected phy-sical and chemical properties of these soils are shown in Tables 1 and 2.

Fertilizers

Fertilizer materials used were UP which is a solid product produced by reacting solid U with merchant-grade wet-process phosphorus acid (0-54-0). The resulting UP [$(NH_2)_2CO{\cdot}H_3PO_4$] product is either granular or crystalline with characteristics of an acid (Achorn, 1984). Other fertilizers were U [$(NH_2)_2CO$] and phosphuric acid (U -.$H_2SO_4{\cdot}H_3PO_4$). Commercial UP grades are 17.5-44.4-0, 46-0-0 and 28-8-0, respectively.

Ammonia Volatilization From Urea Phosphate and Urea

A laboratory experiment utilizing an aeration system was conducted to study the reactions of UP and U in regard to NH_3 volatilization from ammonium-forming nitrogen fertilizers (NH_4^+-N). Three soils representing a wide range of properties (Laveen loam, Hayhook sandy loam and Latene loam) were selected. A 300 g sample of each soil was placed in a quart Mason jar. Rates of application of UP and U ranged from 0 to 200 ppm-N (0, 50, 100 and 200 ppm-N) and were applied either to the surface dry or in solution as evenly as possible or mixed with the soil. Soils were moistened with deionized water up to one bar tension (approximately to the readily available moisture content). This is equivalent to 14.31% for the Laveen, 7.17% for the Hayhook and 13.76% for the Latene soil. Deionized

Table 1. Selected physical and chemical properties of the soils used in the ammonia volatilization and salinity studies.

Soil	Texture	Sand	Clay	pH	EC_e	NO_3-N	Exchangeable Cations meq/100g soil				ESP	CEC
		%		Sat.paste	$dS.m^{-1}$	mg/l	Ca	Mg	Na	K		meq/100g soil
Hayhook	SL	75.0	10.8	6.90	6.83	53.0	8.48	3.45	0.17	0.87	1.83	9.0
Laveen	L	46.4	22.0	7.95	7.37	28.8	47.88	4.11	0.82	0.67	3.32	12.7
Latene	L	51.0	18.0	8.10	0.64	1.6	46.51	3.04	0.33	0.81	2.84	11.3
Pima	L	47.3	22.5	7.90	11.2	18.9	29.63	9.74	6.41	0.99	48.59	35.5
Crot	C	43.3	45.5	9.18	32.0	6.2	51.92	4.47	24.65	1.57	41.32	39.6

Table 2. Water soluble ions for Pima and Crot soils.

Soil	Ca	Mg	Na	K	Total Cations	Cl	SO_4	HCO_3	CO_3	Total Anions	SAR
	meq/L										
Pima	0.94	0.21	9.29	0.21	10.65	3.98	3.43	2.08	0.00	9.49	12.88
Crot	0.29	0.31	26.58	0.17	27.35	12.70	12.19	1.32	0.96	27.17	14.43

water was spread as evenly as possible throughout the surface. For the UP and U solution-treated soils, UP and U were dissolved in the required amount of deionized water and distributed as evenly as possible throughout the soil surface. There were three replications of each treatment.

The jars containing the treated soils were connected to the aeration system (Figs. 1 and 2). A regulated jet of purified (passed through 3N H_2SO_4 solution) and humidified (passed through deionized water) air was passed at 5 cm distance above the soil surface and directed to the side wall of the jar in order to perform a proper mixing of the air in the space above the soil surface inside the jar. The air exiting the jar was passed through 0.5 N H_2SO_4 solution which trapped volatilized ammonia. The air flow rate was 9.81 l/hr/jar, that is equal to approximately 15 air replacement times per hour per jar. Air flow was applied from both ends of the main air line in order to minimize the pressure gradient throughout the main line. The experiment was run at room temperature (approximately 23°C). The trapped NH_3 was determined every 2, 5, 11, 17, 25 and 30 days using the microkjeldahl distillation procedure (Bremner and Edwards, 1960; Bremner, 1961) cited by Black et al. Cumulative milligrams and percent loss were calculated. Net losses, that is milligrams lost from the treatments compared to the untreated soils, were also calculated.

Effect of Urea Phosphate and Leaching on Soil Sodium and Salinity

Two saline-sodic soils (Pima and Crot) were used in this study. A greenhouse-laboratory experiment was conducted in which leaching columns

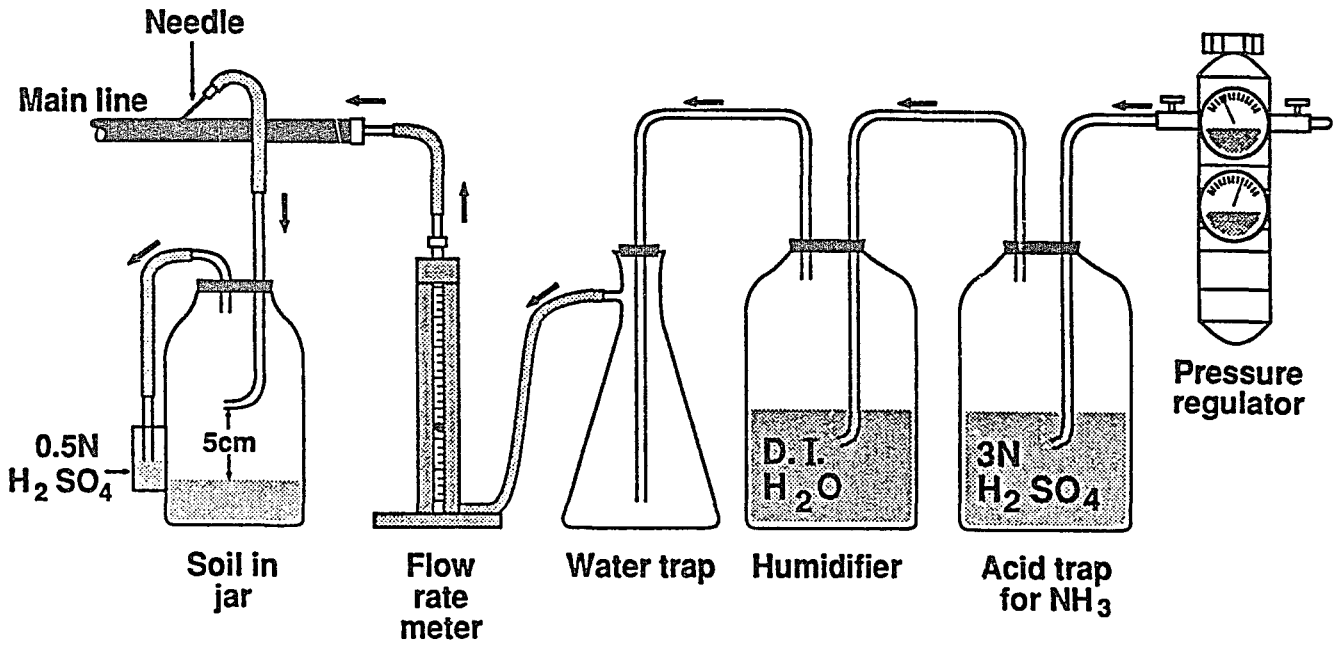
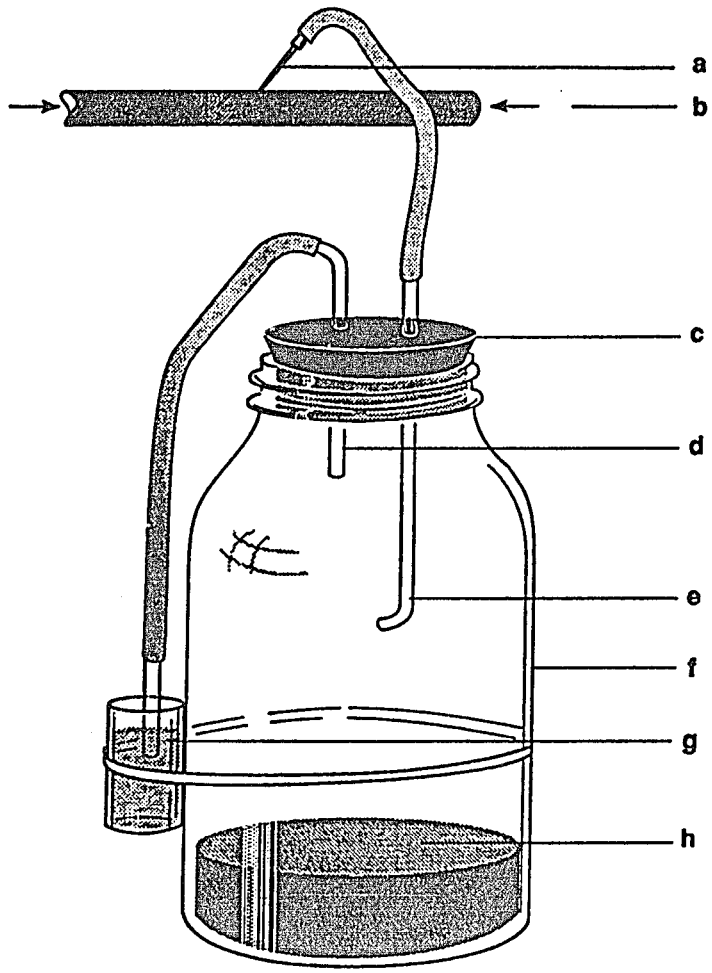


Fig. 1. Diagram of the aeration system used in the ammonia volatilization study.



a. Syringe needle
b. Main air line
c. Rubber stopper
d. Air outlet
e. Air inlet
f. Mason jart
g. Acid trap
h. Treated soil

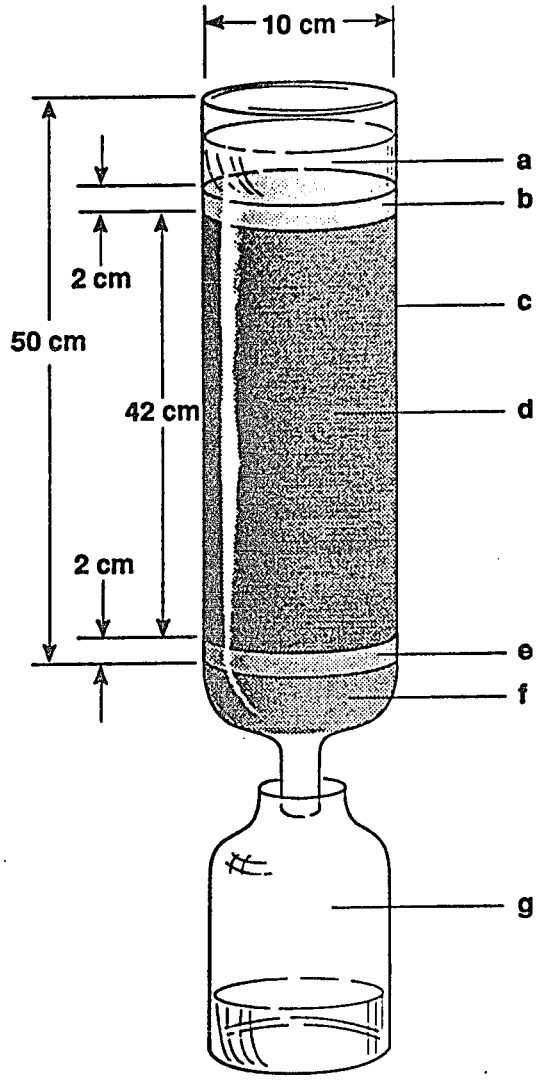
Fig. 2. Aeration unit.

of soils were utilized. Five major treatments (control, UP, Sulfur-Foam (SF), Mixture of UP and SF and Phosphuric solution (PHP) were each applied at two rates (one and two equivalent amounts of the exchangeable Na^+ in the soil), except for the control treated soil, for a total of nine treatments. Sulfur-Foam is a waste-material containing sulfur which has been produced in Iraq at a rate of about 500 tons per day as a by-product of mining and refining sulfur (Dawood, 1980). Table 3 shows the chemical analysis of SF. Phosphuric solution (7.5-26-0-8) is a liquid fertilizer containing nitrogen in the form of U, phosphorus in the form of H_3PO_4 and sulfur in the form of H_2SO_4. The UP-SF mixture was made in order to arrive at the same equivalent amount of sulfuric and phosphoric acids present in the PHP solution. Appendix 1 shows the calculation and the amounts of these materials used in this study. There were four replications for a total of 72 columns.

Four kilograms of soil were packed uniformly by manual packing apparatus in P.V.C. columns of 10 cm inside diameter and 50 cm length. The average soil depth inside the column was 42 cm over a 2 cm fine quartz sand layer. A glass wool sheet covered the drainage hole at the bottom of each column to prevent plugging (Fig. 3). Fine quartz sand was also placed on the soil surface to minimize soil disturbance when applying the leaching water. Soil columns were leached with tap water in an open system. Soil treatments were added and mixed with the top 10 cm of the soil column; followed by a continuous moistening with a one pore volume of leaching water in order to have as uniform moisture and material distribution as possible throughout the soil column. Soils were left for

Table 3. Analysis of Sulfur-Foam material

Content	Percent
Free sulfur soluble in CS_2	79.9
Sulfur insoluble in CS_2	1.57
Carbon	0.43
H_2SO_4	1.33
Ash	14.5
Zn	0.002



a. Leaching water
b. 2 cm fine silica sand layer
c. PVC column
d. 42 cm soil column
e. 2 cm fine silica sand layer.
f. Glass wool sheet
g. Collection bottle

Fig. 3. Soil column component and the dimensions.

2 weeks without leaching, but with adequate moisture, for reaction completion and sulfur oxidation, then leached continuously and the leachate was collected for analysis. Leachate was analyzed subsequently for EC (dSm^{-1}) until the EC of the leachate was close to the EC of the leaching water and additional leaching would have little affect on the EC value of the leachate.

After leaching was stopped each soil column was air dried, ground to pass a 2 mm sieve and analyzed for selected chemical properties.

CHAPTER 4

RESULTS AND DISCUSSION

Ammonia Volatilization From Urea Phosphate and Urea

Ammonia loss by volatilization is only one of several ways N can be lost from the plant environment. The intensity of this form of N loss will be discussed in this chapter. A Randomized Complete Block Design (RCB) with split-split plot analysis was used. Only the cumulative net percent N loss at the 30th day (end of the experiment) data were analyzed statistically. An attempt was made to analyze the data as a split-split-split plot with a four way interaction namely, soils, rates of fertilizer application, method of fertilizer application and type of fertilizer as main plots, sub-plots, sub-sub plot and sub-sub-sub plot, respectively. Because of the difficulty of interpreting the four-way interaction (which was statistically significant), the experiment was subsequently analyzed as three separate experiments, one for each soil. Each of these experiments will be discussed separately and a conclusion will be drawn depending on effect of the soil characteristics on NH_3 loss behavior.

Ammonia Volatilization From Hayhook Soil

The NH_3 volatilization loss from U and UP applied to the soil over time is shown in Table 4 and Figures 4, 5, 6, and 7. Analysis of variance with the least significant difference (LSD) procedure was used to evaluate the results. The statistical analysis of the rates of fertilizer

Table 4. Net cumulative N loss as NH_3 from U and UP applied to Hayhook soil.

N Rate (ppm)	Method of N Appli.	Net Cumulative N Loss Per 2 days mg	%	5 days mg	%	11 days mg	%	17 days mg	%	25 days mg	%	30 days mg	%
						Urea Phosphate							
50	Mix.	0.01	0.09	0.04	0.23	0.07	0.45	0.08	0.51	0.10	0.66	0.13	0.83
	Sol.	0.02	0.12	0.05	0.36	0.10	0.69	0.12	0.78	0.15	1.01	0.19	1.25
	Sur.	0.03	0.18	0.07	0.47	0.13	0.86	0.16	1.06	0.20	1.35	0.24	1.59
100	Mix.	0.01	0.04	0.04	0.12	0.07	0.22	0.08	0.25	0.11	0.38	0.14	0.48
	Sol.	0.02	0.06	0.06	0.20	0.13	0.42	0.16	0.52	0.19	0.64	0.24	0.79
	Sur.	0.02	0.08	0.11	0.37	0.24	0.80	0.30	0.98	0.37	1.22	0.42	1.40
200	Mix.	0.02	0.04	0.05	0.09	0.09	0.15	0.12	0.21	0.15	0.25	0.19	0.32
	Sol.	0.03	0.04	0.05	0.08	0.10	0.17	0.15	0.25	0.20	0.33	0.24	0.41
	Sur.	0.03	0.05	0.16	0.27	0.71	1.18	0.93	1.55	1.08	1.80	1.19	1.99
						Urea							
50	Mix.	0.13	0.85	0.17	1.11	0.23	1.53	0.24	1.59	0.28	1.87	0.30	1.98
	Sol.	0.45	3.03	0.51	3.39	0.70	4.65	0.75	4.99	0.88	5.85	0.91	6.03
	Sur.	0.89	5.94	1.22	8.11	1.76	11.73	1.83	12.23	1.90	12.67	1.93	12.88
100	Mix.	0.22	0.74	0.35	1.18	0.59	1.98	0.70	2.32	0.74	2.48	0.80	2.65
	Sol	1.15	3.83	1.82	6.08	2.38	7.95	2.52	8.41	2.65	8.84	2.71	9.02
	Sur.	2.63	8.78	3.82	12.72	4.63	15.45	4.84	16.13	5.00	16.65	5.05	16.84
200	Mix.	0.90	1.51	1.97	3.29	3.71	6.19	4.20	6.99	4.74	7.91	5.02	8.37
	Sol.	3.92	6.53	6.14	10.23	8.44	14.06	9.14	15.23	9.81	16.35	10.07	16.78
	Sur.	6.49	10.82	9.31	15.52	11.87	19.78	12.64	21.07	13.33	22.22	13.57	22.61

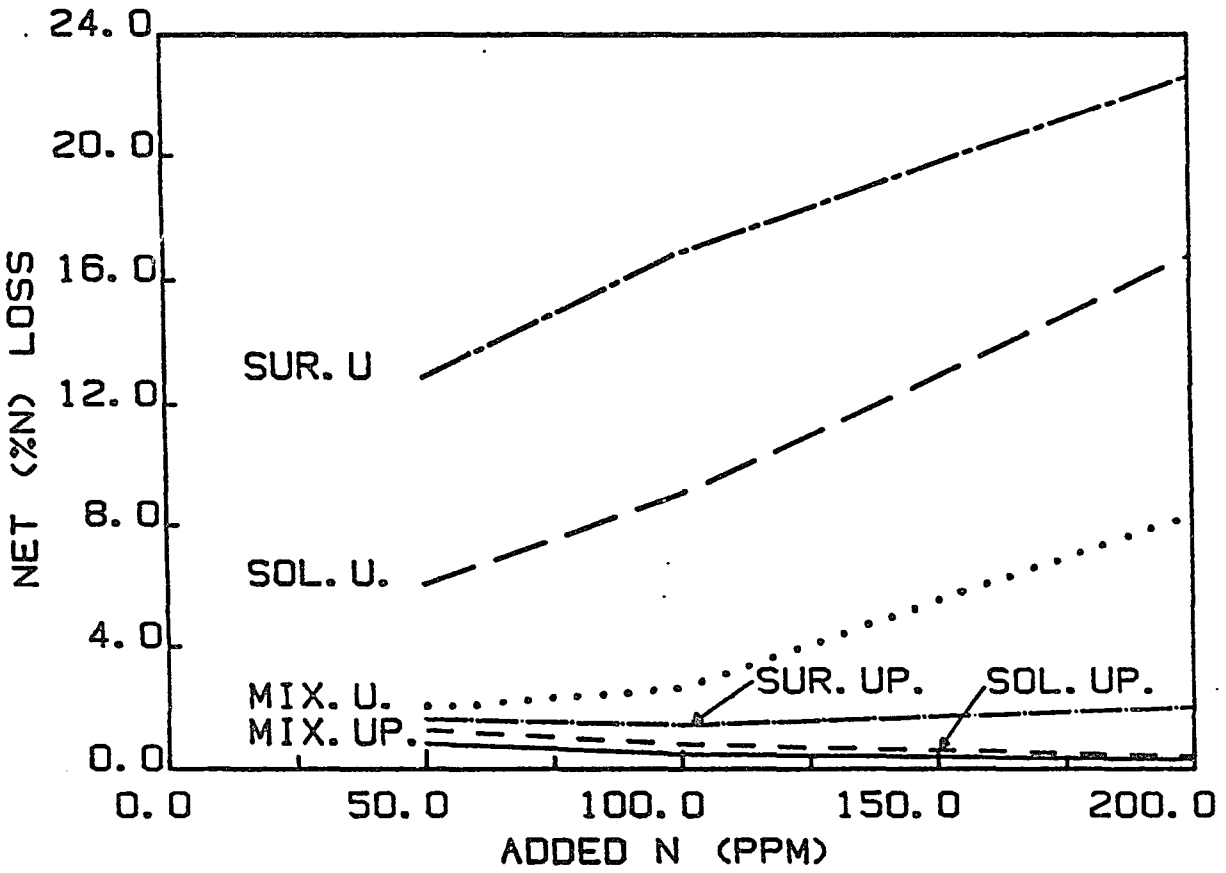


Fig. 4. Net cumulative percent N loss from U and UP added to Hayhook soil at different rates and methods of application.

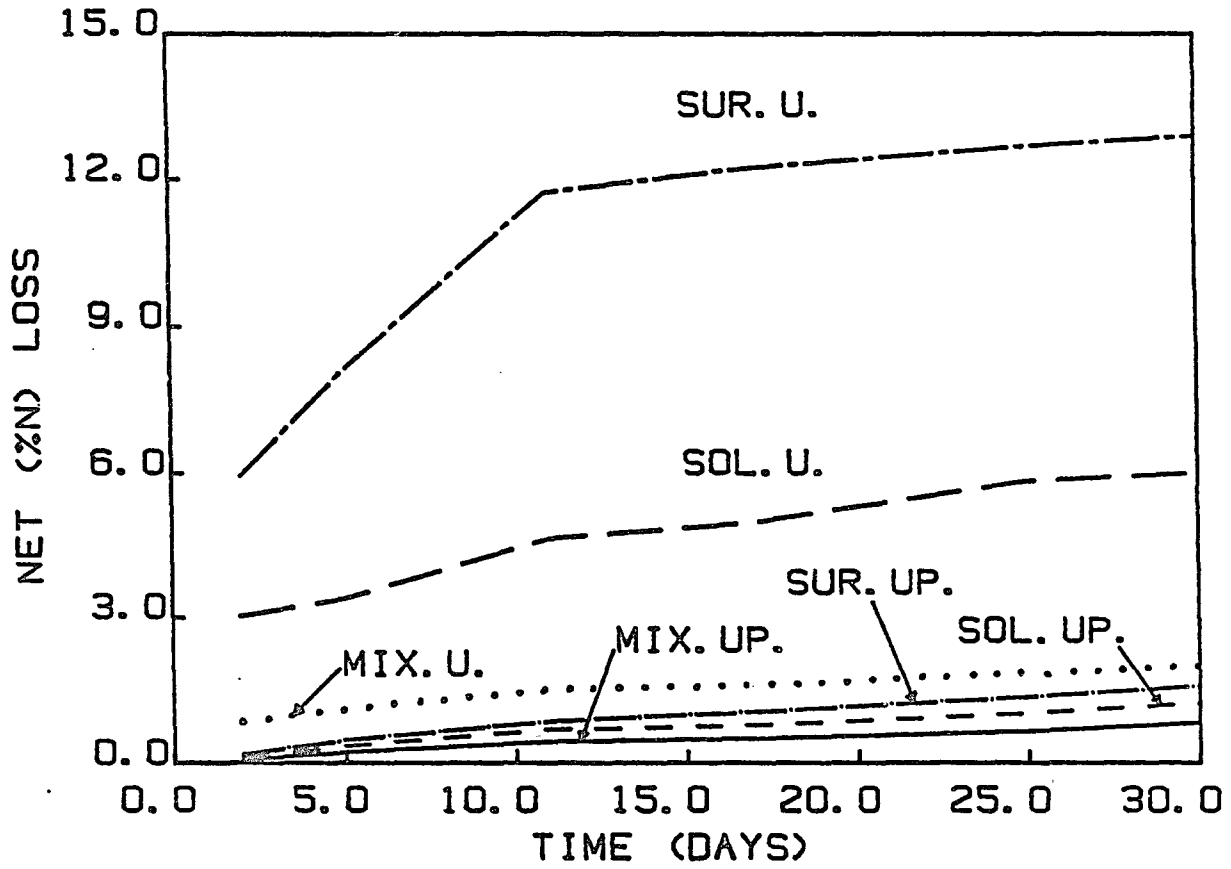


Fig. 5. Net cumulative percent N loss from U and UP applied to Hayhook soil (50 ppm-N) at different methods of application.

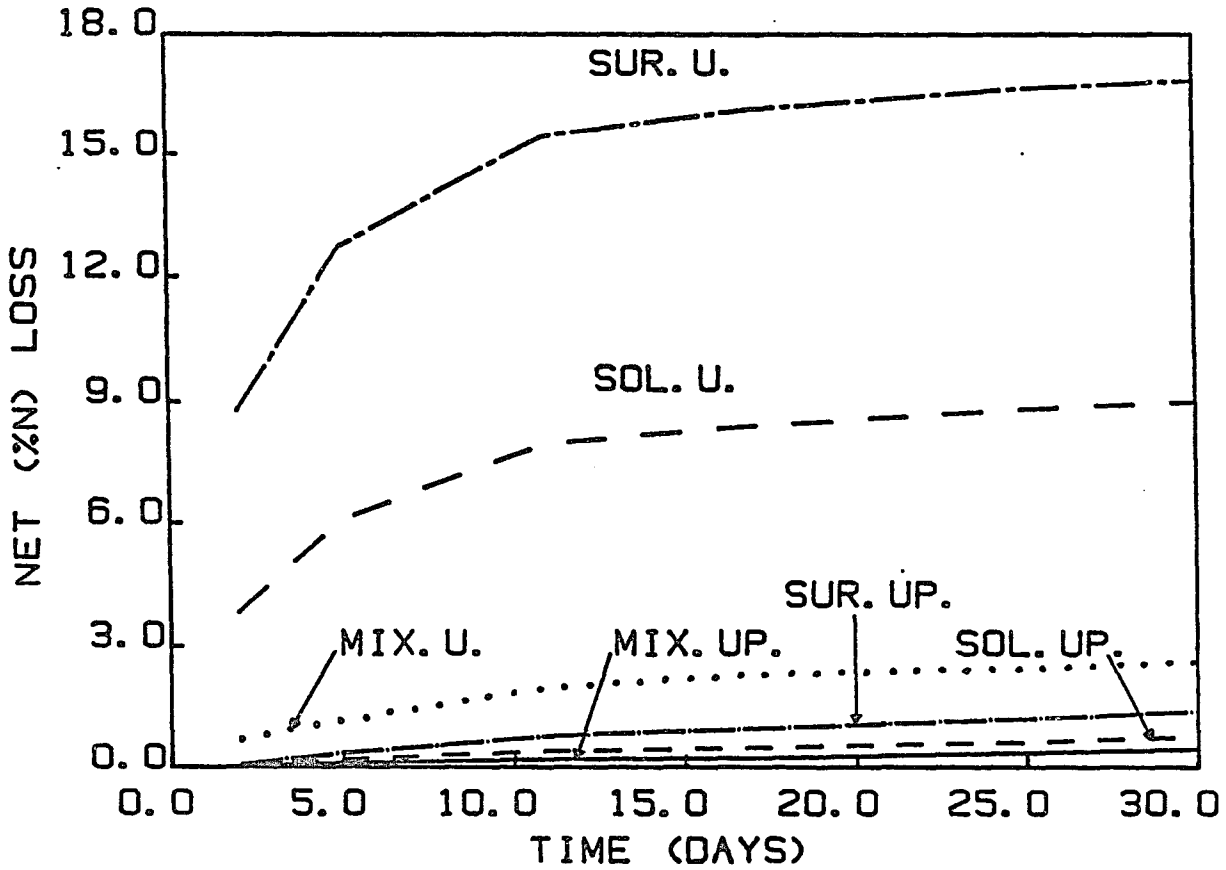


Fig. 6. Net cumulative percent N loss from U and UP applied to Hayhook soil (100 ppm-N) at different methods of application.

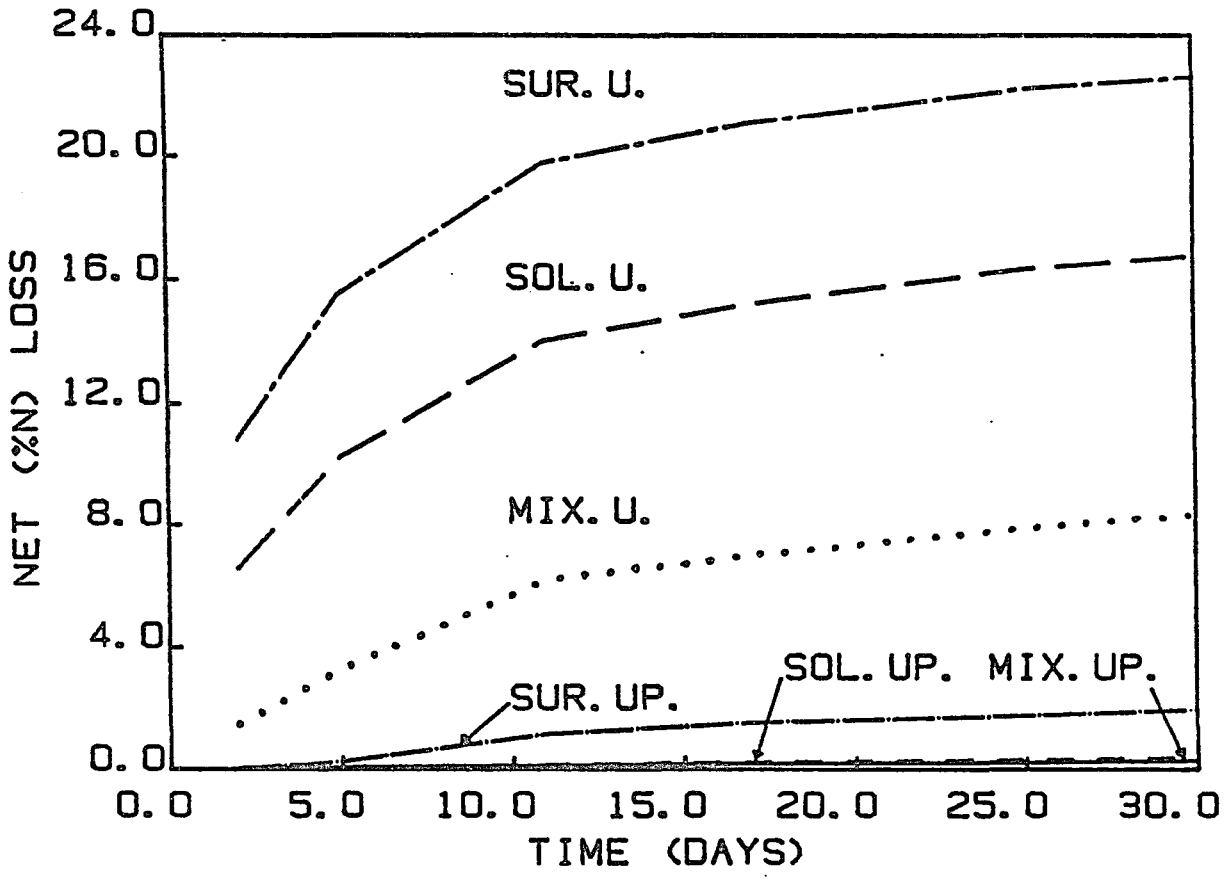


Fig. 7. Net cumulative percent N loss from U and UP applied to Hayhook soil (200 ppm-N) at different methods of application.

application (rates), methods of fertilizer application (methods), fertilizer type (types), rates x type interaction and methods x type interactions, were significant (at the 95% confidence level). No significant difference was obtained between (a) rates x methods interaction and (b) rates x methods x type interaction.

There was no significant difference in percent N loss when UP was applied at rates of 50, 100 and 200 ppm-N. Doubling the application rate of UP doubled the absolute quantity (in mg-N loss) between 100 and 200 ppm-N rates, and increased the absolute quantity by 1.5 and 3 times between 50 and 100 ppm-N and 50 and 200 ppm-N, respectively, but did not increase the percentage loss significantly. This was because increasing UP application rate increases phosphoric acid additions which will have an acidifying effect and buffer the increase in soil pH resulting from hydrolysis of urea in the soil. The phosphoric acid in UP retards enzymatic hydrolysis of urea by soil urease and reduces gaseous loss at urea-N as NH_3. The phosphoric acid found in the compound will inhibit soil urease activity when applied to the soil (Bremner and Douglas, 1971). With more H^+ buffering capacity, extra H^+ ions are available for the urea hydrolysis which will result in smaller increases in soil pH and less NH_4^+ dissociation to $NH_3 + H^+$. Consequently, the NH_3 volatilization potential will decrease with increased H^+ buffering capacity.

The statistical analysis also indicated that there was a significant difference between treatments when urea was applied to the soil at rates of 50, 100 and 200 ppm-N. Urea fertilization rate influenced the amounts of NH_3 loss. Greater loss with increased

fertilization can be anticipated. In addition, as fertilization rate increased, both the absolute quantity and net percentage loss of N also increased. When the fertilization rate was increased from 50 to 100 ppm-N, nitrogen loss as NH_3 increased by 2.7 fold (as absolute quantity) and by 1.4 (as net percentage). When the fertilization rate was increased from 100 to 200 ppm-N, ammonia volatilization increased by nearly 3.4 and 1.7-fold as absolute quantity and net percentage, respectively. Nitrogen loss as NH_3 increased by nearly 9.2 and 2.3-fold, as absolute quantity and net percentage respectively, when the urea application rate was increased from 50 to 200 ppm-N. In all cases of application rates, the amount of volatilized NH_3 was greater from urea than urea phosphate. This increase may be the result of higher NH_3 concentration because of greater urea hydrolysis with a corresponding increase in pH. Thus, the soil was unable to adsorb and hold high concentrations of NH_3. With UP, there is less urea hydrolysis, lower pH, and less NH_3 loss resulted. Ammonia loss from U was 5.7, 10.7 and 17.7-fold greater than UP when N was applied at rates of 50, 100 and 200 ppm, respectively. Even when N was applied at 50 ppm rate as urea, the amount of volatilized NH_3 was significantly higher than when N was applied as UP at rates 100 and 200 ppm by 3.9 and 1.9-fold as absolute quantity and 7.8 and 7.7-fold as percentage, respectively. A similar difference in the results was obtained when urea was applied at rates of 100 and 200 ppm-N with respect to UP application rates.

The statistical analysis shows a similar trend when U and UP were applied to the surface (dry or in solution) or when mixed with the soil to that when they were applied at different rates (50, 100 and 200 ppm-

N). No significant difference was obtained when UP was applied to the soil by the three different methods, whereas, applying dry U-N to the surface, showed significantly higher loss by 1.6 and 4.0-fold as percentage (1.6 and 16.1 as absolute quantity) than when applied to the surface in solution or when mixed with the soil, respectively. The amount of N loss in the form of volatilized NH_3 increased significantly in the following order when U was applied dry to the surface > in solution to the surface > mixed with the soil. After U is applied to the surface, water is absorbed and hydrolysis to ammonium carbonate [$(NH_4)_2CO_3$] occurs and ammonia becomes free to volatilize into the atmosphere. When U is mixed with the soil, NH_3 is contained by the soil, captured in the soil solution, and can be bound to soil colloids as NH_4^+ before loss to the atmosphere can occur. Because Hayhook soil is coarse in texture and low in cation exchange capacity (CEC), adding U in solution to the surface will move it deep enough in the soil as water percolates through the soil and less NH_4^+ ions will be adsorbed or held at soil surface. Nitrogen loss as NH_3 occurs when NH_4^+ ion is at or near the soil surface and comes to equilibrium with soil basicity to form free NH_3 in excess of the NH_3 holding capacity of the soil. Because of the low buffering capacity of Hayhook soil and since NH_3 loss is controlled by pH as follows:

$$NH_4^+ + OH^- \longleftrightarrow NH_3 + H_2O$$

$$\longrightarrow pH \longrightarrow$$

the pH of the localized zone or the microsite at the surface of a fertilizer particle contacting a soil particle surface can change little

or markedly depending on the soil buffering capacity, concentration of reactants and the nature of the reaction.

Like other microbial systems, the urease enzyme is active over a given pH range. Urease functions effectively at soil pH in which plants grow, but loses its hydrolytic activity at low pH values; therefore, NH_3 loss depends on the final pH of the micro and macro-system. Also, the rate of NH_3 loss is a function of the partial pressure difference in the atmosphere and soil air which is in equilibrium with NH_4^+ concentration in soil solution and on soil particles. The statistical analysis shows that the data are in agreement with this reasoning. The H_3PO_4 in UP lowered soil pH, inhibited U hydrolysis and lower NH_3 losses resulted than when N was applied as U in terms of rates or methods of application.

Most of the N was lost in the form of volatilized NH_3 during the first 2 days after U was applied in solution to the surface or mixed with the soil at the 50 ppm-N rate and when mixed with the soil at 100 ppm-N rate (Figs. 5 and 6), whereas most of the loss occurred within the first 11 days when U was applied dry to the surface (50, 100 and 200 ppm-N) or in solution to the surface (100 and 200 ppm-N)(Figs. 5, 6 and 7). On the other hand, a gradual N loss as NH_3 resulted when UP was applied to the soil surface dry or in solution or when mixed with the soil at all rates (50, 100 and 200 ppm-N) throughout the 30-day experimental period (Figs. 5, 6 and 7). The H_3PO_4 would tend to reduce losses from the low pH UP because of its additional buffering capacity against a rise in pH.

Decreased volatilization from UP-treated soil was due to delayed dissolution and hydrolysis of urea in soil.

Ammonia Volatilization
From Laveen Soil

The NH_3 volatilization loss from U and UP applied to the soil are shown in Table 5 and Figures 8, 9, 10 and 11. Analysis of variance with the LSD procedure was used to evaluate the results. The statistical analysis showed that rates of fertilizer application were significantly different. Differences between (a) methods, (b) type and (c) methods and type interaction were significant (at 95% confidence level). No significant difference was obtained between (a) rates and (b) methods x type interaction and finally (c) rates x methods x type interaction.

The statistical analysis indicated that there was no significant difference in the amount of N lost as NH_3 when U and UP were applied to the soil at 50 and 100 ppm-N. When N was applied at the 200 ppm rate, as U or UP, the amount of volatilized NH_3 was significantly higher by 1.7 and 2.3-fold as percentage (3.4 and 9.2-fold as absolute quantity) than when N was applied at 100 and 50 ppm rates, respectively. The amount of N loss in the form of volatilized NH_3 was influenced by fertilization rate. As fertilization rate increased, greater NH_3 concentration (Fig. 8) due to greater urea hydrolysis and the subsequent increase in soil pH.

The statistical analysis also indicated that there was no significant difference in the amount of N lost as volatilized NH_3 when both urea and UP were mixed with the soil and when UP was added in solution to the soil surface. Only about 1.22, 1.15 and 1.41% (0.18, 0.17 and 0.42 mg)

Table 5. Net cumulative N loss as NH_3 from U and UP applied to Laveen soil.

N Rate (ppm)	Method of N Appli.	Net Cumulative N Loss Per 2 days mg	2 days %	5 days mg	5 days %	11 days mg	11 days %	17 days mg	17 days %	25 days mg	25 days %	30 days mg	30 days %
						Urea Phosphate							
50	Mix.	0.03	0.19	0.07	0.45	0.12	0.77	0.12	0.79	0.12	0.79	0.12	0.83
	Sol.	0.01	0.07	0.05	0.34	0.13	0.84	0.16	1.07	0.17	1.15	0.17	1.16
	Sur.	0.02	0.11	0.15	0.98	0.36	2.41	0.42	2.77	0.42	2.78	0.42	2.81
100	Mix.	0.03	0.09	0.16	0.52	0.29	0.97	0.32	1.07	0.32	1.07	0.32	1.07
	Sol.	<0.01	0.01	0.06	0.21	0.26	0.87	0.35	1.16	0.35	1.17	0.35	1.18
	Sur.	0.02	0.05	0.15	0.49	0.68	2.25	0.83	2.78	0.85	2.82	0.88	2.94
200	Mix.	0.01	0.05	0.30	0.49	0.76	1.27	0.86	1.44	0.90	1.50	0.93	1.54
	Sol.	<0.01	<0.01	0.06	0.10	0.63	1.05	0.98	1.63	1.10	1.83	1.16	1.94
	Sur.	0.01	0.01	0.18	0.30	1.12	1.86	1.76	2.93	1.97	3.29	2.01	3.35
						Urea							
50	Mix.	0.16	1.07	0.18	1.21	0.19	1.23	0.20	1.34	0.22	1.43	0.23	1.50
	Sol.	0.24	1.59	0.30	2.03	0.32	2.16	0.33	2.18	0.32	2.31	0.36	2.41
	Sur.	0.34	2.29	0.44	2.91	0.47	3.15	0.47	3.16	0.48	3.21	0.50	3.33
100	Mix.	0.17	0.56	0.21	0.70	0.22	0.74	0.28	0.93	0.28	0.94	0.29	0.96
	Sol.	0.40	1.34	0.60	2.01	0.68	2.28	0.68	2.28	0.69	2.28	0.69	2.28
	Sur.	0.42	1.40	0.80	2.67	0.94	3.14	0.94	3.14	0.96	3.19	0.97	3.23
200	Mix.	0.24	0.40	0.37	0.62	0.44	0.73	0.57	0.95	0.65	1.09	0.71	1.19
	Sol.	0.55	0.92	1.51	2.52	1.98	3.30	2.01	3.35	2.02	3.37	2.05	3.41
	Sur.	0.59	0.99	1.77	2.96	2.60	4.33	2.66	4.43	2.67	4.45	2.68	4.46

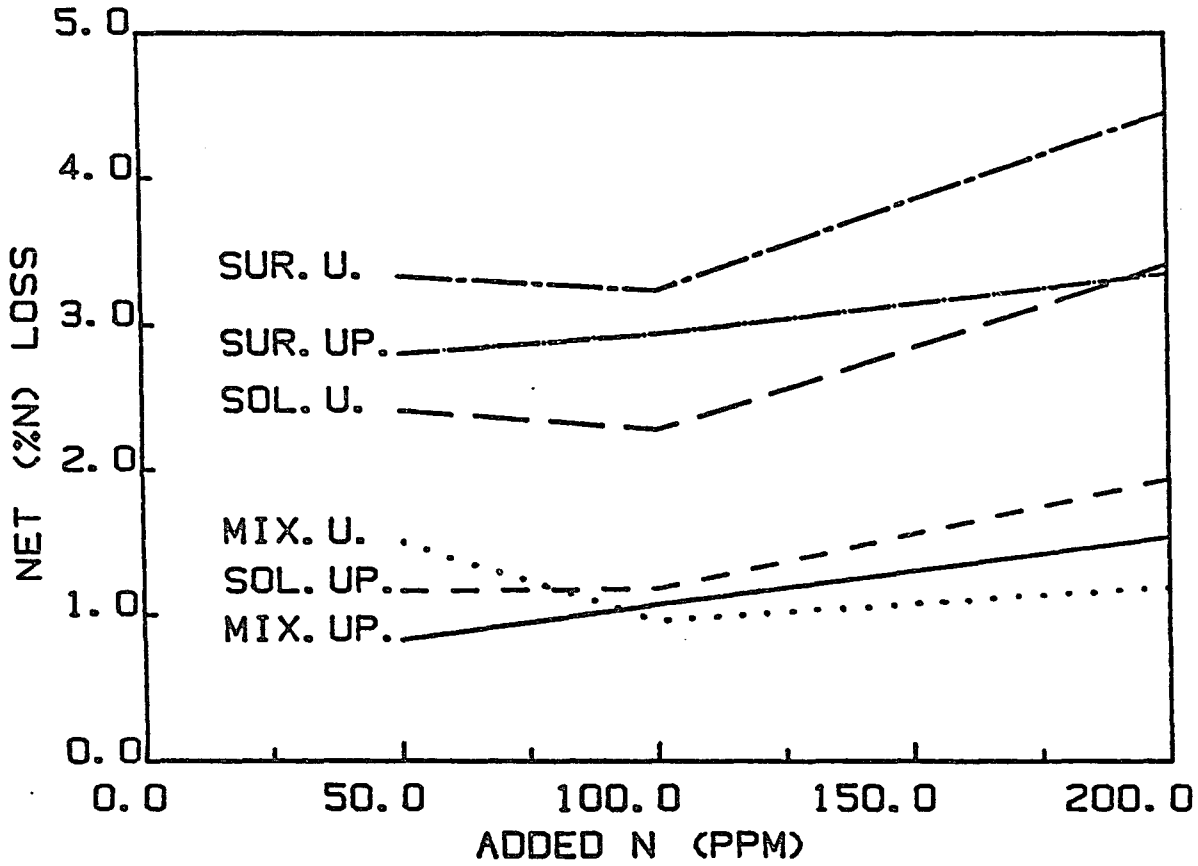


Fig. 8. Net cumulative percent N loss from U and UP added to Laveen soil at different rates and methods of application.

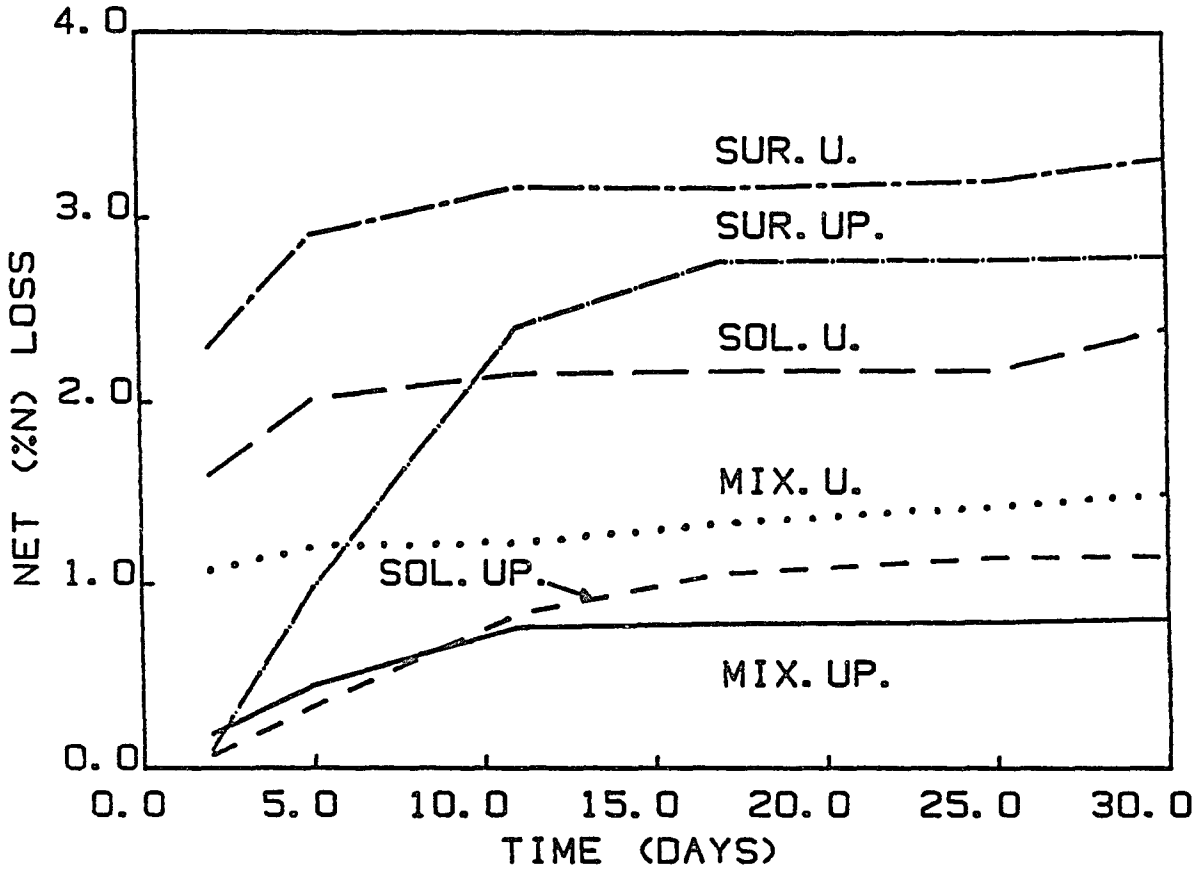


Fig. 9. Net cumulative percent N loss from U and UP applied to Laveen soil (50 ppm-N) at different methods of application.

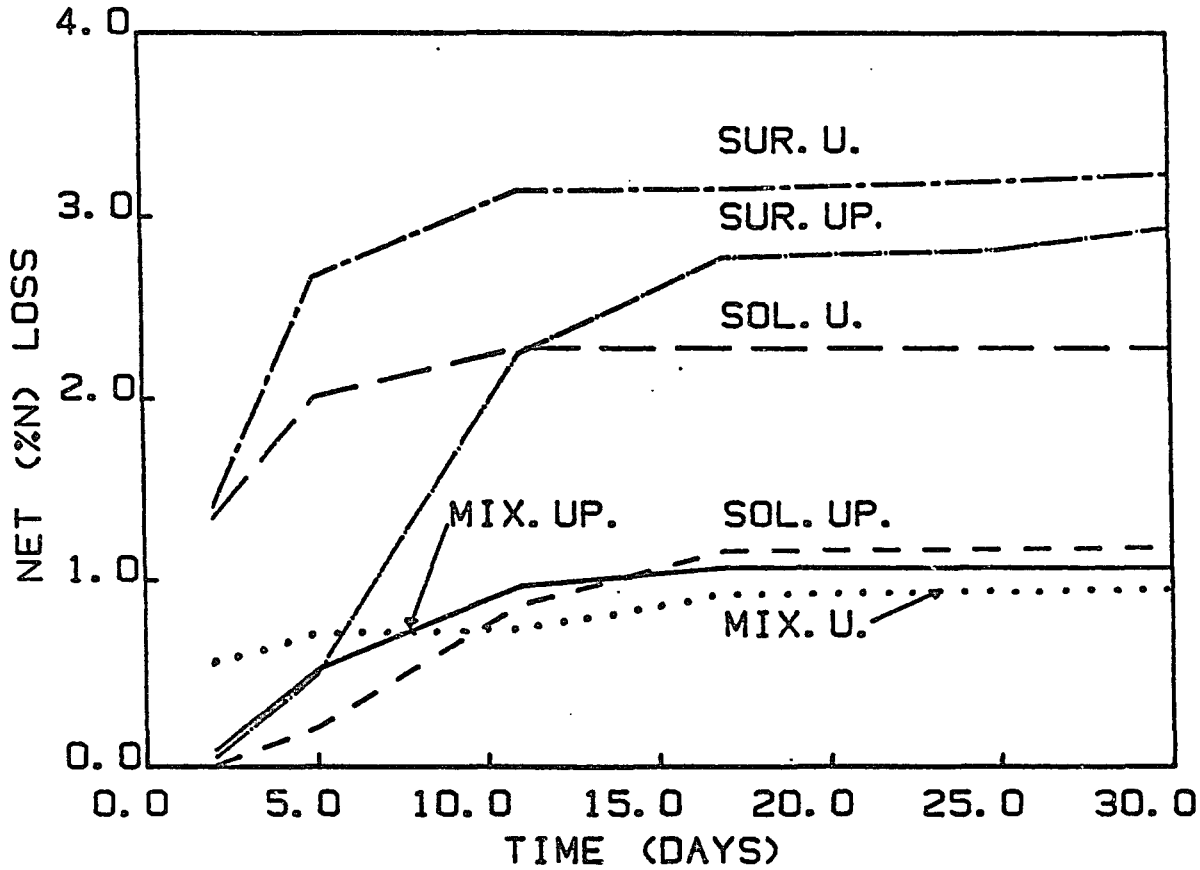


Fig. 10. Net cumulative percent loss from U and UP applied to Laveen soil (100 ppm-N) at different methods of application.

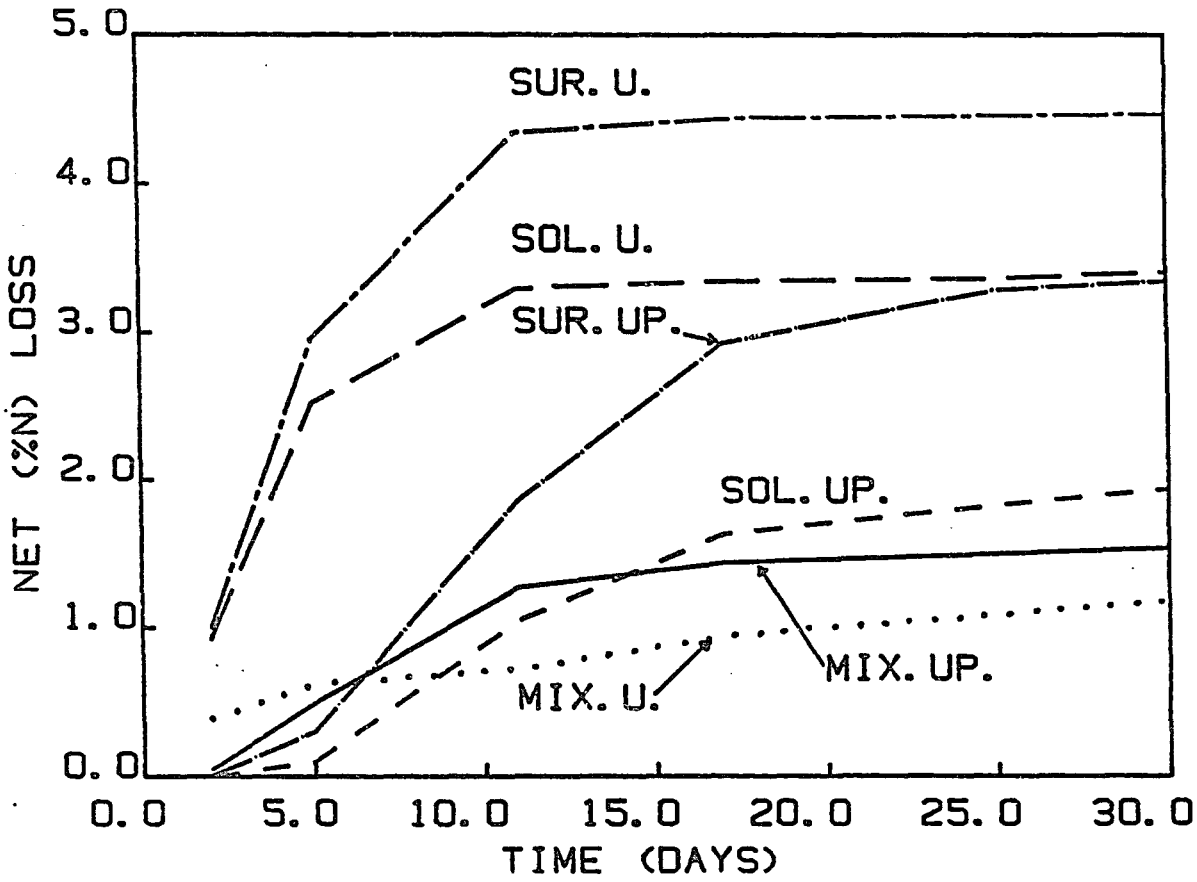


Fig. 11. Net cumulative percent N loss from U and UP applied to Laveen soil (200 ppm-N) at different methods of application.

of the added N, respectively were lost. Intermediate losses were obtained when U or UP were applied to the surface in solution (2.68%) or dry (3.07%), respectively. These losses were not significantly different, but they were significantly higher than when U or UP was mixed with the soil or when UP was applied to the surface in solution. The highest loss (statistically significant) was obtained when U was applied dry to the surface (3.67%).

Generally, higher losses were obtained with dry application of the fertilizer to the surface than in solution or mixing the fertilizer with the soil. The rate of fertilizer diffusion into the soil determines the concentration remaining at the surface. Incorporating (mixing) the fertilizer into the soil to a depth of 5 cm or more will unlikely result in NH_3 volatilized (Fenn and Kissel, 1973). Surface application of NH_4^+ or NH_4^+-forming fertilizers to soils with moderate or high CEC may restrict diffusion to depths which allow protection from volatilization loss.

Most of the N was lost between 2 and 5 days when applied as urea (Figs. 9, 10 and 11). When N was applied as UP, NH_3 loss was gradual, especially when mixed with the soil or when applied in solution to the surface at all rates of application (50, 100 and 200 ppm-N). When UP was applied dry to the surface, most of the loss occurred between the first 11 to 17 days at all rates. When U was applied to the surface of the soil dry or in solution at rates of 100 and 200 ppm-N, most of the loss occurred within the first 11 days.

Ammonia Volatilization
From Latene Soil

The NH_3 volatilization loss from U and UP applied to the soil is shown in Table 6 and Figures 12, 13, 14 and 15. Analysis of variance with the LSD procedure was used to evaluate the results. The statistical analysis showed that there was no significant difference when both U or UP were mixed with the soil and when UP was applied to the soil surface in solution at all rates of fertilizer application. About 0.19, 0.24, 0.31, 0.20, 0.39, 0.27, 0.51, 0.69 and 0.72% of the added N was lost for these three treatments, respectively. The least amount of N was volatized from these treatments. Doubling the rate of fertilizer application increased the rate of N loss as absolute quantities, but not the percentage losses (Table 5).

Nitrogen applied in solution to the soil surface at rates of 100 and 200 ppm as UP and 50 ppm as U showed no significant difference in the amount of volatilized NH_3. About 0.69, 0.72 and 1.77% of the added N was lost, respectively. Loss of N from the latter treatment was significantly higher than when U or UP were mixed with the soil at all rates and when UP was applied in solution to the soil surface at 50 ppm-N rate by 9.3, 7.4, 5.7, 8.9, 4.5, 6.6 and 3.5-fold, respectively. No significant difference, with higher rate of N loss, was found when U was applied to the soil surface in solution at 50 and 100 ppm-N rates and when UP was applied dry to the soil surface at the 50 ppm-N rate.

Applying U in solution to the soil surface at the 200 ppm-N rate resulted in a significant N loss, in the form of volatilized NH_3, which was

Table 6. Net cumulative N loss as NH_3 from U and UP applied to Latene soil.

N Rate (ppm)	Method of N Appli.	Net Cumulative N Loss Per 2 days mg	%	5 days mg	%	11 days mg	%	17 days mg	%	25 days mg	%	30 days mg	%
						Urea Phosphate							
50	Mix.	0.01	0.04	0.01	0.07	0.02	0.11	0.02	0.15	0.03	0.20	0.03	0.20
	Sol.	0.05	0.30	0.05	0.39	0.06	0.43	0.07	0.47	0.07	0.49	0.08	0.51
	Sur.	0.06	0.43	0.14	0.94	0.18	1.21	0.24	1.59	0.28	1.88	0.30	2.03
100	Mix.	0.04	0.14	0.08	0.28	0.09	0.30	0.10	0.33	0.11	0.35	0.12	0.39
	Sol.	0.05	0.18	0.11	0.37	0.17	0.57	0.19	0.63	0.20	0.66	0.21	0.69
	Sur.	0.37	1.24	0.84	2.81	1.06	3.54	1.11	3.69	1.13	3.75	1.14	3.79
200	Mix.	0.10	0.17	0.14	0.23	0.16	0.26	0.16	0.27	0.16	0.27	0.16	0.27
	Sol.	0.08	0.14	0.33	0.55	0.41	0.69	0.42	0.70	0.42	0.71	0.43	0.72
	Sur.	0.31	0.51	1.45	2.42	2.20	3.67	2.25	3.76	2.27	3.79	2.30	3.81
						Urea							
50	Mix.	0.01	0.05	0.01	0.07	0.02	0.13	0.02	0.15	0.03	0.19	0.03	0.19
	Sol.	0.13	0.87	0.17	1.13	0.20	1.31	0.26	1.71	0.26	1.76	0.27	1.77
	Sur.	0.20	1.34	0.34	2.26	0.47	3.14	0.53	3.55	0.57	3.79	0.59	3.96
100	Mix.	0.02	0.05	0.05	0.15	0.06	0.19	0.06	0.20	0.06	0.20	0.07	0.24
	Sol.	0.36	1.19	0.59	1.96	0.65	2.18	0.65	2.18	0.67	2.24	0.68	2.25
	Sur.	1.17	3.89	1.73	5.75	1.98	6.60	2.01	6.68	2.03	6.76	2.04	6.81
200	Mix.	0.05	0.09	0.14	0.23	0.17	0.28	0.18	0.30	0.18	0.30	0.19	0.31
	Sol.	0.96	1.59	1.74	2.90	1.86	3.10	1.87	3.12	1.88	3.14	1.89	3.15
	Sur.	2.43	4.05	5.62	9.36	7.19	11.99	7.20	12.00	7.21	12.01	7.22	12.03

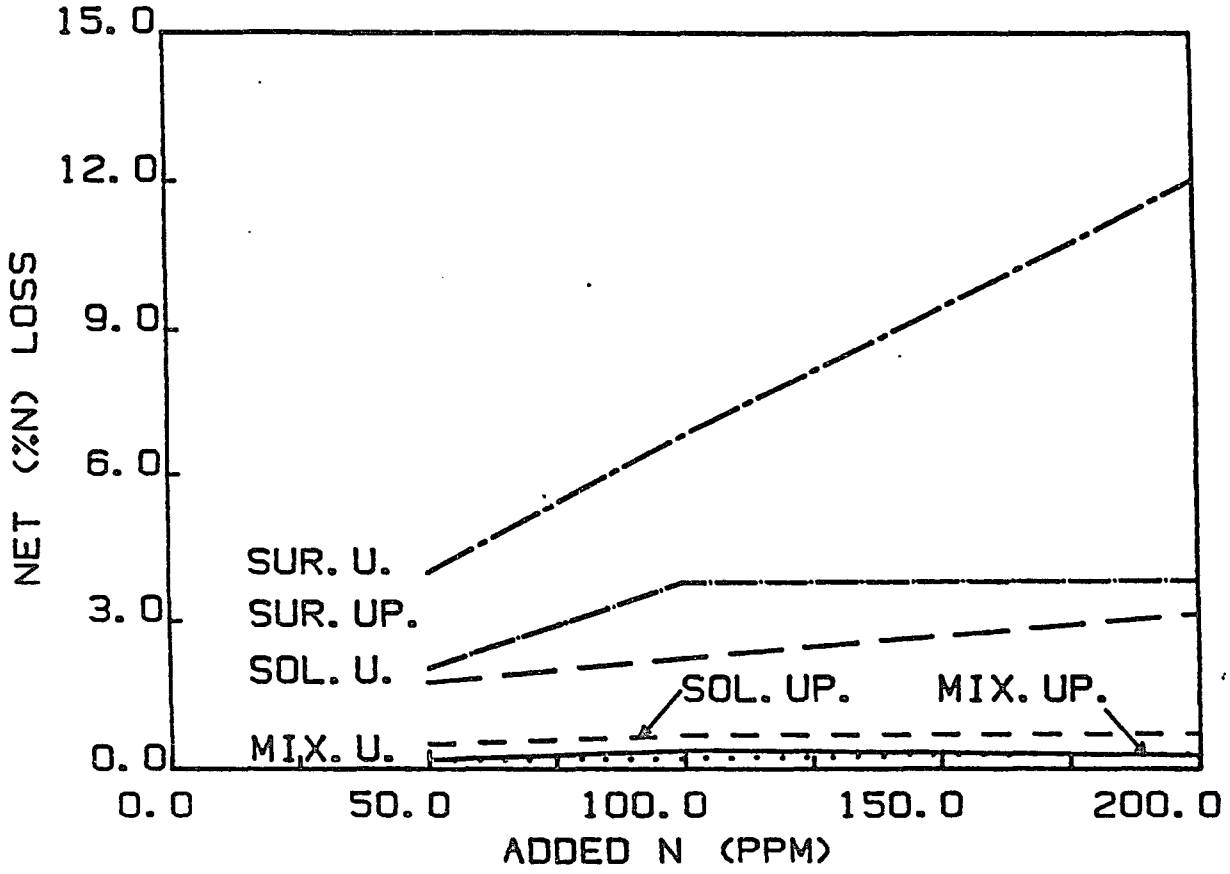


Fig. 12. Net cumulative percent N loss from U and UP applied to Latene soil at different rates and methods of application.

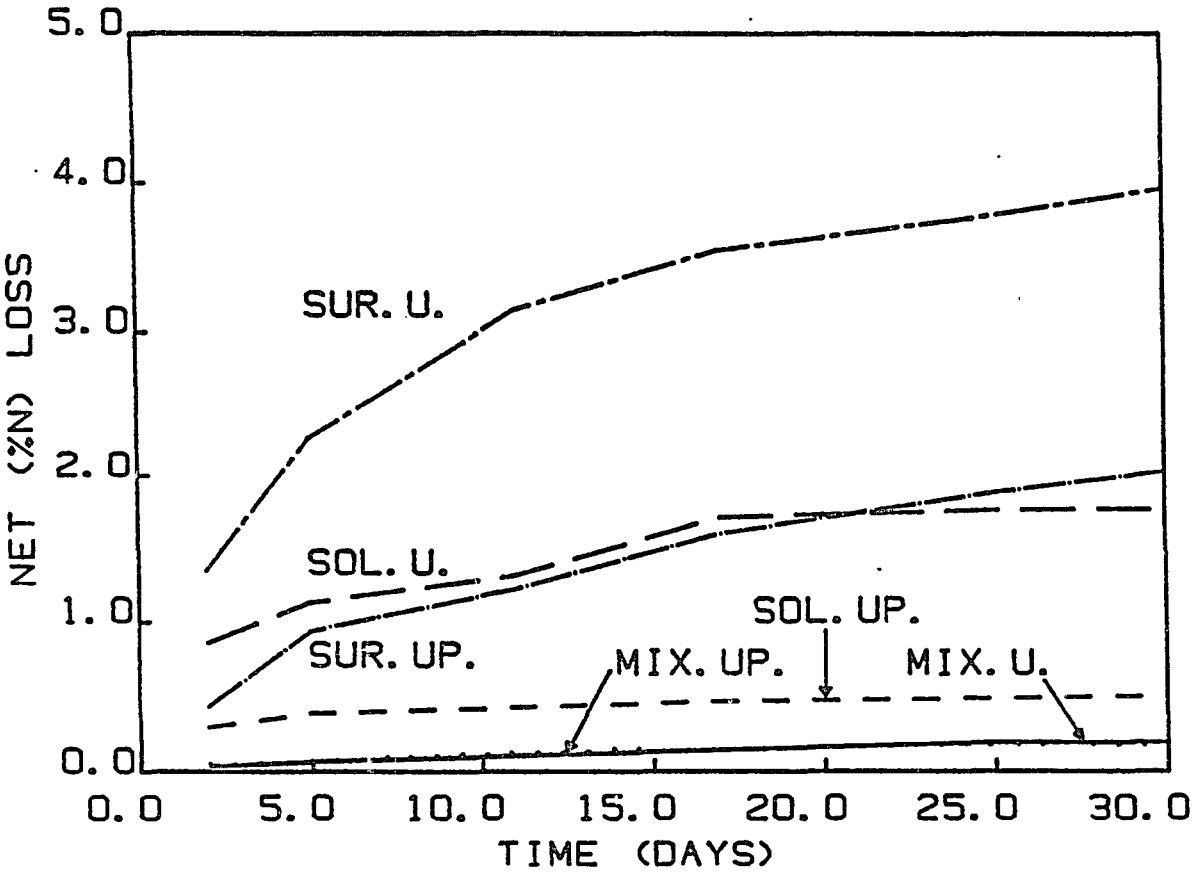


Fig. 13. Net cumulative percent N loss from U and UP applied to Latene soil (50 ppm-N) at different methods of application.

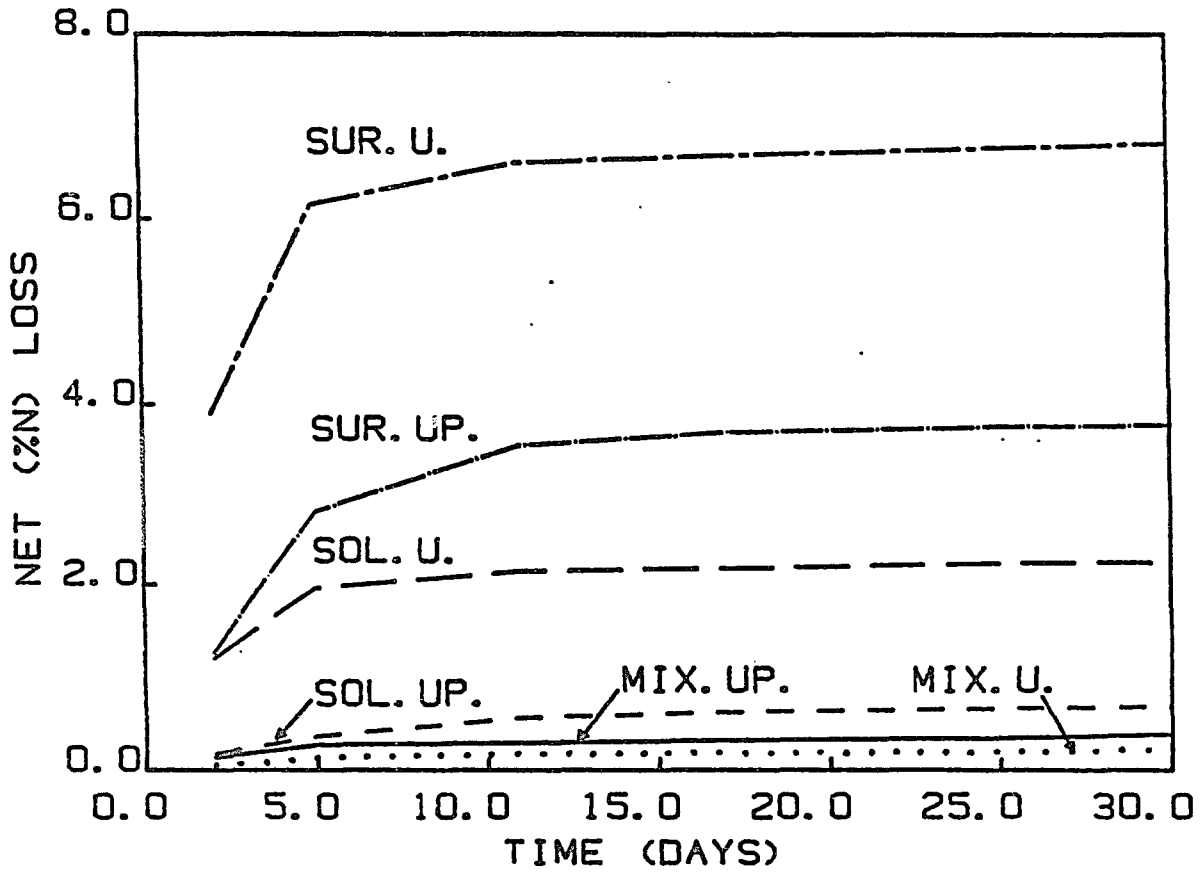


Fig. 14. Net cumulative percent N loss from U and UP applied to Latene soil (100 ppm-N) at different methods of application.

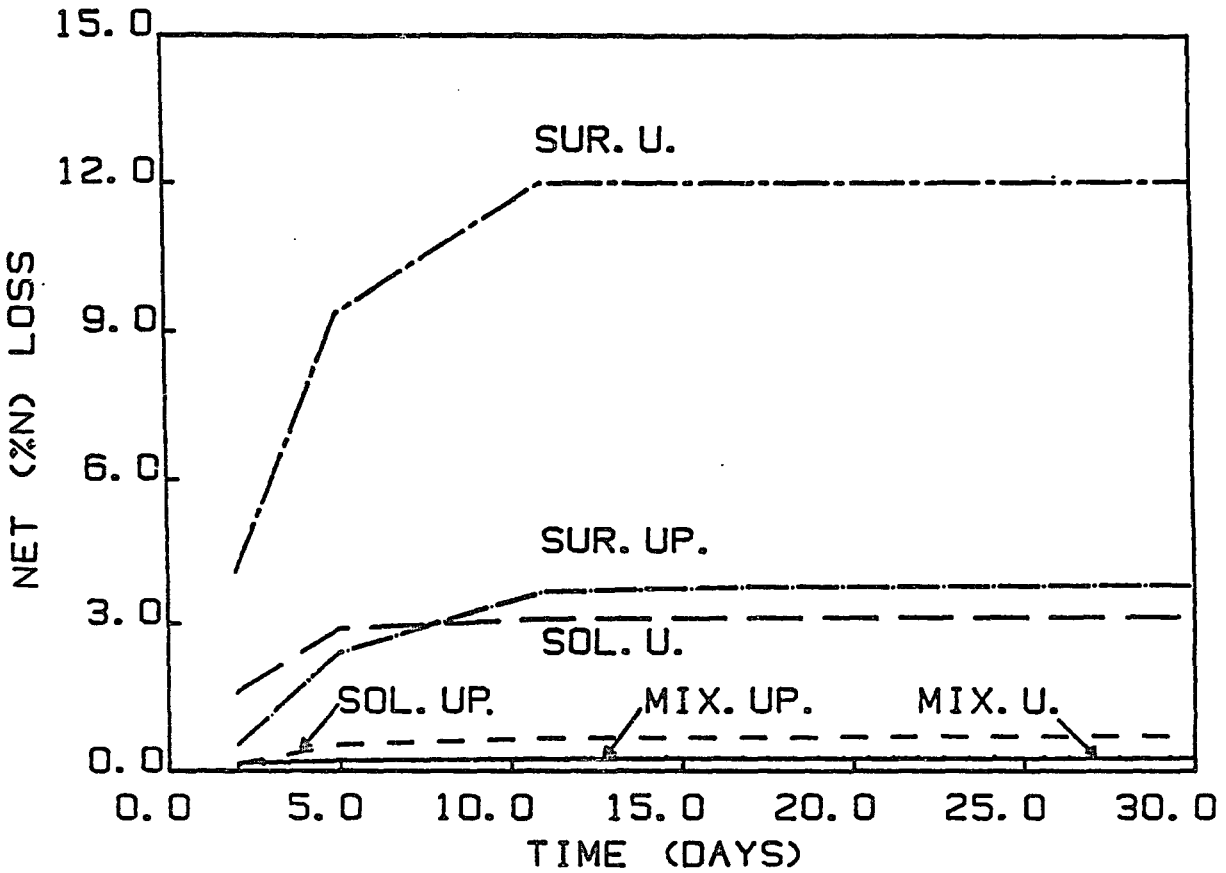


Fig. 15. Net cumulative percent N loss from U and UP applied to Latene soil (200 ppm-N) at different methods of application.

higher by 1.8 and 1.6-fold than when U or UP was applied in solution or dry to the soil surface at the 50 ppm-N rate, respectively. Nosignificant difference was found at the 100 ppm-N rate. About 3.15 and 3.96% of applied N as U to soil surface either in solution or dry, at 200 and 50 ppm-N, respectively, was lost, whereas, 3.79 and 3.81% of the applied N as UP dry to the surface, at 100 and 200 ppm-N, was lost. There was no significant difference between those treatments. Significantly higher N losses were obtained when U was applied dry to the soil surface at the 100 ppm-N rate. The highest amount of N loss as volatilized NH_3 was statistically obtained when U was applied dry to the surface at the 200 ppm-N rate with 12.03% (7.22 as absolute quantity) of the added N lost.

Generally, higher N losses in the form of NH_3 were found when U or UP were applied dry to the soil surface than in solution or mixing the fertilizer with the soil (Fig. 12). Minimum loss occurred when U or UP was mixed with the soil and when UP was applied in solution to the soil surface. A linear continuous loss of N was found when U was applied to the surface either dry or in solution, with much greater loss obtained with dry application to the soil surface. A sharp increase in the N loss from UP occurred when applied dry to the surface up to 100 ppm-N (but the loss was less than when U was applied dry, and higher when U was applied in solution to the soil surface (Fig. 12).

A similar trend of N loss was found when U or UP was applied at the three different (50, 100 and 200 ppm-N) rates with time (Figs. 13, 14 and 15). A much less and gradual N loss occurred when UP was applied compared to U at each rate and method of application. Most of the N loss occurred

during the first 5 days when both U and UP were applied to the soil, except when U was applied dry to the surface, N loss continued from 11 to 17 days.

Effect of Urea Phosphate and Leaching on Soil Sodium and Salinity

Saline and alkali soil conditions reduce the value and productivity of considerable areas of land in the world. Despite the fact that the problem is an old one, a lot of information in the technical literature is available on this subject; there is need for continued research on this problem and the interrelations to crop production on these soils (Allison, et al., 1954).

Thirteen soil chemical properties, namely electrical conductivity (EC_e), pH, soluble sodium (Na_s), calcium (Ca_s), and magnesium (Mg_s), in ppm and meq/L, and sodium adsorption ratio (SAR), from the soil saturated paste extract, and the exchangeable sodium (Na_{ex}), calcium (Ca_{ex}), magnesium (Mg_{ex}), and exchangeable sodium percent (ESP) were evaluated in this study for each soil. A Randomized Complete Block with split-plot design was used for the analysis of variance in the statistical analysis of the results. The LSD procedure (at 95% confidence level) was also used for mean comparison. Each of the two soils was statistically analyzed separately because of the different characteristics of the soils. A list of symbols which are used in the test for the various treatments is given in Table 7.

Table 7. List of symbols.

Symbol	Description
SF 1	Sulfur-Foam applied at rate of one equivalent amount of the Na_{ex}.
SF 2	Sulfur-Foam applied at rate of two equivalent amounts of the Na_{ex}.
Mix 1	Mixture of SF and UP applied at rate of one equivalent amount of the Na_{ex}.
Mix 2	Mixture of SF and UP applied at rate of two equivalent amounts of the Na_{ex}.
UP 1	Urea Phosphate applied at rate of one equivalent amount of the Na_{ex}.
UP 2	Urea Phosphate applied at rate of two equivalent amounts of the Na_{ex}.
PHP 1	Phosphoric Solution applied at rate of one equivalent amount of the Na_{ex}.
PHP 2	Phosphoric Solution applied at rate of two equivalent amounts of the Na_{ex}.
Cont.	Control

Pima Soil

The statistical analysis of the water soluble (saturated paste extract) and exchangeable parameters showed that there was no significant difference between rates of fertilizer (as amendment) application, (1 and 2 equivalent amounts of Na_{ex}). A marked decrease in soil pH occurred with increasing rate of application (Table 8). Doubling the rate of fertilizer or amendment application decreased soil pH about 0.2 to 0.7 units, depending on material. The decrease in pH was because of the acidic nature of the materials used in the experiment. It was also found that there were significant differences between treatments and their interaction with rate of application. A decrease in soil pH occurred in the order of PHP, UP, MIX and SF and Control treatment. All differences were significant except for the SF and Control treatment. This was because conditions were not favorable for sulfur oxidation in the sulfur waste material. Phosphoric solution has the highest acidic nature because it contains both phosphoric and sulfuric acid and produced the lowest soil pH. Urea phosphate, on the other hand, contains phosphoric acid, and mixing it with SF was significantly more effective in reducing soil pH than using SF alone.

In terms of EC measurement, no significant difference was found between interaction of treatments with rate of application. The statistical analysis also indicated a significant difference among treatments. Lower EC values were found in the order of PHP, UP, MIX, SF and Control. No significant difference was found between PHP, UP and MIX treatments, but they were significantly lower than SF and Control

Table 8. Means of measured water soluble parameters as affected by treatment and rates of application in Pima soil.

Treatment	pH	EC	$Na_{s.}$		$Ca_{s.}$		$Mg_{s.}$		SAR
		$dS.m^{-1}$	ppm	meq/L	ppm	meq/L	ppm	meq/L	
SF 1	8.55	1.10	337	14.7	63.9	3.20	8.2	0.69	13.4
SF 2	8.34	1.04	382	16.6	18.4	0.92	2.5	0.21	22.2
MIX 1	8.11	1.00	236	10.3	42.5	2.12	7.9	0.66	8.6
MIX 2	7.51	0.76	99.2	4.3	52.1	2.61	11.4	0.95	3.3
UP 1	7.68	0.81	83.5	3.6	38.2	1.91	7.9	0.66	3.2
UP 2	6.91	0.76	60.3	2.6	55.6	2.78	15.8	1.32	1.8
PHP 1	7.30	0.72	54.2	2.3	56.2	2.81	12.5	1.04	1.7
PHP 2	6.81	0.85	45.6	1.9	71.2	3.56	15.9	1.32	1.2
Control	8.48	1.15	311	13.5	65.0	3.25	8.6	0.72	13.3

treatments, except for MIX treatment. Also, no significant difference was obtained between MIX, SF and Control treatments.

Applications of acid containing materials increases soil acidity, solubilize more salts, including relatively insoluble salts. Leaching will result in lower EC values with the increase in acidic nature of the material (Table 8).

A similar trend was obtained when soluble soil cations (Na_s, Ca_s, and Mg_s) were analyzed statistically in ppm or meq/L. The statistical analysis indicated that there was a significant difference between treatments themselves and their interaction with rate of application. Soluble sodium (Na_s) concentration decreased in the order of PHP, UP, MIX, Control and SF when measured in ppm, and UP, PHP, MIX, Control and SF when measured in meq/L. The statistical analysis also showed that, in both cases, there was no significant difference between PHP and UP (lowest concentration). MIX treatment was significantly lower than Control and SF but higher than PHP and UP in both cases. No significant difference was obtained between the Control and SF treatments when measured in meq/L, but SF treatment was significantly higher than Control treatment when measured in ppm.

Soluble calcium concentration showed no significant difference with all variables and their interactions when measured in both ppm and meq/L. Soluble magnesium concentration showed an increase in the order SF, Control, MIX, UP, and PHP treated soil. Only PHP and UP treated soil resulted in significantly higher Mg_s concentration than SF treated soil.

The PHP treatments resulted in the highest Mg_s concentration among all treatments except UP where it was not significantly different.

Soluble cations (Na_s, Ca_s and Mg_s) measured in meq/L were used to calculate SAR. The statistical analysis of SAR showed that there was no significant difference between variables and their interactions. Since the SAR is defined as $Na^+ / \sqrt{Ca^{2+} + Mg^{2+} / 2}$ (in meq/L), therefore any decrease in Na_s is accompanied by an increase in the Ca_s and/or Mg_s resulting in lower SAR values. Because Ca_s was not significantly different and Mg_s values slightly different for most of the treatment (when measured in meq/L), therefore there was not much effect of cations concentration to produce differences among SAR values. Table 8 shows the mean values of the water soluble parameters.

The statistical analysis of the exchangeable parameters (Na_{ex}, Ca_{ex}, Mg_{ex}, and ESP) showed that there was no significant difference between rates of application (1 and 2 eq, the amount of Na_{ex}). The ESP was calculated from the SAR values using the equation 100(-0.0126 + 0.01475 SAR)/1+(-0.0126 + 0.01475 SAR) (Allison et al., 1954). The statistical analysis of the ESP showed that there was a significant difference between treatments and interaction of treatments with rate of application. The decrease in ESP was in the order of PHP, UP, MIX, Control and SF. No significant difference was obtained between PHP and UP treatments, but they produced significantly the lowest overall ESP values. The MIX treatment produced significantly lower ESP values than the Control treatment which was also significantly lower than the SF treatment (Table 9).

Table 9. Means of measured exchangeable parameters as affected by treatment and rates of application in Pima soil.

Treatment	Na_{ex}	Ca_{ex}	Mg_{ex}	ESP
	meq/100 g soil			
SF 1	3.88	28.0	2.61	15.4
SF 2	3.67	25.6	2.48	24.0
MIX 1	2.67	24.3	3.14	10.1
MIX 2	1.30	21.8	3.60	3.5
UP 1	1.53	21.0	3.28	3.3
UP 2	1.15	19.2	3.95	1.3
PHP 1	1.58	23.3	3.71	1.2
PHP 2	0.99	19.6	3.24	0.6
Control	4.04	25.4	2.51	15.2

The statistical analysis of the Na_{ex} showed that there was no significant difference between interaction of the treatments and rate of application. It was also found that there was a significant difference between treatments themselves. The Control and SF treatments showed no significant difference, resulting in the highest level of Na_{ex}. The level of Na_{ex} decreased in the order PHP, UP, MIX, SF, and Control. No significant difference also, was found between MIX and UP treatments. These treatments showed lower Na_{ex} levels than SF and Control treatment. The lowest level of Na_{ex} resulted from treating the soil with PHP. The latter treatment was found to be not significantly different from UP treatment (Table 9). It was obvious from the results that, as the acidic nature of the treatment increases (PHP>UP>MIX>SF>Control), the Na_{ex} concentration decreases. This is because of the solubilization of the Ca^{2+} from the relatively insoluble Ca-compounds such as $CaCO_3$ or $CaSO_4$. Calcium ions will replace the Na_{ex} on the exchange sites, then the Na^+ will be leached out.

No significant difference was found between treatments and/or their interaction with rate of application on the Ca_{ex}. Exchangeable Ca was influenced by the soluble or even slightly soluble Ca compounds present in the soil, such as $CaSO_4$ and $CaCO_3$ or possibly $Ca\text{-}PO_4$. These Ca compounds may become more soluble by adding these acid containing fertilizers and affect the actual values of Ca_{ex}. The Mg_{ex} results showed that there was a significant difference among treatments and the interaction of treatments with rate of applications. An increase in the amount of Mg_{ex} was in the order UP, PHP, MIX, SF, and Control. This shows an

opposite relationship to that of the Na_{ex}. Increasing the amount of Ca_{ex} and or Mg_{ex}, decreased the Na_{ex} level in soil. This was because of the exchange reactions phenomenon and the leaching of Na^{+} after it was being displaced by Ca^{2+} and/or Mg^{2+}, resulting in improved water penetration through the soil column and leaching efficiency.

Crot Soil

The statistical analysis of the water soluble parameters (saturated paste extract) showed a different trend for Crot soil than Pima soil. Soil pH values showed significant differences between rate of applications, treatments, and the interaction between treatments and rate of application. Except for SF and Control treatments, a marked decrease in soil pH occurred with doubling the rate of fertilizer (as amendment) application (Table 10). Soil pH decrease was in the order PHP, UP, MIX, SF, and Control with PHP producing significantly the lowest pH value. No significant difference was obtained between SF and Control treatments only. The other treatments were significantly different from each other. This was because of the acidic nature of the materials and the poor conditions for S oxidation.

No significant difference was obtained between rate of applications when measuring soil EC, but there was a significant difference between treatments and interaction of treatments with rates of application. The EC values increased in the order MIX, UP, PHP, SF, and Control. No significant difference was found between MIX and UP treatments, producing the lowest EC values. Also, no significant difference was found between

Table 10. Means of measured water soluble parameters as affected by treatment and rates of application in Crot soil.

Treatment	pH	EC	Na_s.		Ca_s.		Mg_s.		SAR
		$dS.m^{-1}$	ppm	meq/L	ppm	meq/L	ppm	meq/L	
SF 1	9.26	20.9	3183	138	24.8	1.24	6.9	0.58	175
SF 2	9.25	17.7	3310	144	18.2	0.91	5.9	0.50	181
MIX 1	7.99	0.8	104	4.52	14.1	0.70	38.5	3.21	4.31
MIX 2	7.79	0.8	99.3	4.32	17.2	0.86	11.8	0.99	4.58
UP 1	7.80	1.2	93.8	4.08	10.2	0.51	8.4	0.70	5.57
UP 2	7.26	0.8	81.0	3.52	20.8	1.04	36.7	3.06	2.54
PHP 1	7.57	2.0	125	5.43	137.2	6.86	99.0	8.25	2.18
PHP 2	6.60	11.5	57.6	2.51	589.8	29.50	766	63.81	0.38
Control	9.39	21.2	3529	153	17.3	0.86	4.03	0.34	178

SF and Control treatments, producing the highest EC values (Table 10). Sodium, Ca^{2+} and Mg^{2+} salts are the major contributors to soil salinity and/or alkalinity in saline and alkali soils. Values of all these three cations were shown to be significantly affected by treatments. Calcium and Mg ions showed a similar relationship, significantly different, but opposite to that of the Na in terms of rates of application and interaction of treatments x rates of application. That was true when these cations were measured in ppm and meq/L.

No significant difference was found in Na concentrations between UP, PHP, and MIX treatments (resulting in lower values than SF and Control treatments). Control and SF treatments, on the other hand, showed no significant difference between them, resulting in higher values than UP, PHP, and MIX treatments. Calcium and Mg, on the other hand, showed a similar pattern. No significant difference was found between UP, MIX, Control, and SF treatments. Only PHP was significantly higher than the rest of the treatments. Sodium Adsorption Ratio (SAR) showed the same relationship to that of Na_s. No significant difference was found between rate of application and the interaction of treatments with rate of application. Treatments showed to be significantly different with PHP, UP and MIX treatments (no significant difference between them) having lower SAR values than SF and Control treatments, which were not significantly different. This was obvious because of the slight differences in Ca_s and Mg_s as affected by treatments and the more pronounced treatments effect of Na_s concentrations. Since SAR measurement

depends on Na_s, Ca_s, and Mg_s concentrations (meq/L), therefore, it showed a similar pattern to that of Na_s.

The statistical analysis of the exchangeable parameters (Na_{ex}, Ca_{ex}, Mg_{ex}, and ESP) showed that there was no significant difference between rates of application (1 and 2 eq. the amount of Na_{ex}). As with the Pima soil, ESP was calculated from SAR values. The ESP showed a similar pattern to that of the Na_s, Na_{ex}, and SAR. No significant difference was found in the interaction between treatments x rates of application. Significantly lower values were obtained from PHP, UP and MIX treatments than from SF and Control treatments. The Na_{ex} showed the same relationship mentioned above (Table 11).

The Ca_{ex} and Mg_{ex} showed different relationships in the interaction of treatments x rates of application. It was significantly different with Ca_{ex}, but no significant difference was found with Mg_{ex}. Treatments showed significant effects on the values of both cations (Ca_{ex} and Mg_{ex}), but at a different order for each cation.

The statistical analysis of Ca_{ex} showed that there was no significant difference between UP, SF, MIX, and PHP treatments, producing higher values than the Control treatment. It was also found that Control and PHP treatments were not significantly different in their effect on Ca_{ex} concentrations, producing lower values than MIX, SF, and UP treatments. Exchangeable Ca was influenced by the soluble or even slightly soluble Ca compounds present in the soil, such as $CaSO_4$ and $CaCO_3$ or possibly Ca-PO_4. These Ca compounds may become more soluble by adding these acid containing fertilizers and affect the actual values of Ca_{ex}. The statistical

Table 11. Means of measured exchangeable parameters as affected by treatment and rates of application in Crot soil.

Treatment	Na_{ex}	Ca_{ex}	Mg_{ex}	ESP
	meq/100 g soil			
SF 1	31.1	23.1	2.65	69.8
SF 2	28.5	39.2	3.67	71.8
MIX 1	16.0	19.0	4.39	4.76
MIX 2	16.9	37.3	7.23	5.18
UP 1	16.6	41.5	7.82	6.49
UP 2	15.1	23.6	8.09	2.42
PHP 1	15.9	30.2	6.66	1.92
PHP 2	14.3	15.6	5.14	-0.71
Control	29.9	14.6	1.95	74.1

analysis of Mg_{ex} showed three different groups of treatment effect. Control and SF treatments were not significantly different with lower values than PHP and MIX treatments, which were not significantly different, with values higher than Control and SF but less than UP treatment (the latter treatment was significantly higher in Mg_{ex} concentration than the rest of treatments).

Any decrease in Na_{ex} was accompanied by an increase in the Ca_{ex} and/or Mg_{ex} resulting in lower ESP values (Table 11). This was true when soil was treated with an acidic product (PHP, UP, and MIX). This relationship was based on the dissolution of $CaCO_3$ and the consequent displacement of Na_{ex} by the released Ca and/or Mg on the exchange sites and due to the improved water penetration, resulting from $CaCO_3$ solubilization, Na salts will be leached away and more Ca and/or Mg will be adsorbed on the exchange sites. When cations of unequal valence are present in the soil solution, the higher valence cation will tend to displace the cations of lower valence from the exchanger phase (Ali, 1981).

CHAPTER 5

SUMMARY AND CONCLUSIONS

The major difficulty in studies such as these is the use of artificial laboratory systems which do not duplicate field conditions. Such synthetic systems are susceptible to several sources of error. One has to be very careful in obtaining homogenous soil and equal soil homogeneity compaction in the masor jars or the soil columns. Since all soils were sampled from different sites, some may be under cultivation and some may not, and were taken from the top 30 cm. of the land, there might be variations in the chemical and/or physical characteristics of each soil. Soil heterogeneity may be minimized by grinding, sieving and mixing, but still, there may be some variation between soil in jars or columns. The various degrees of soil compaction, because of the use of hand compaction method, may affect fertilizer penetration depth, pore size, percent porosity and/or continuity of pores which will affect NH_3 exchange between soil pores and the atmosphere. The soil compaction may also affect water infiltration rate and the leaching efficiency through the soil column. It would seem that the use of undisturbed soil cores taken from the field through the desired depth should provide a more comparable basis for making such studies (Ali, 1981).

Ammonia Volatilization From Urea Phosphate and Urea

The extent to which NH_3 losses were influenced by $CaCO_3$ content, soil texture, fertilizer type (U and UP), and the rate (0, 50, 100 and 200

ppm-N) and method of N application (surface dry or in solution and mixed) was examined on three soils (Hayhook SL, Laveen L and Latene L) using an aeration system. Volatilized NH_3 was trapped in the H_2SO_4 solution and analyzed for N periodically until minimum losses occurred.

In all cases, when applying U or UP to each soil, NH_3 loss increases with increasing rate of N application. Applying N to the surface, especially dry than in solution, resulted in higher N loss in the form of volatilized NH_3 than when mixed with the soil. The order of N loss increased as the fertilizer was applied to the surface dry > in solution which was > when mixed with the soil. Most of the N loss occurred within the first 5 days, followed by a minimum N loss which occurred during the next 2 weeks. As a general trend, less losses were obtained from UP than U treated soils. A similar pattern of N loss was found between the three soils, as affected by treatments, but with different values.

Hayhook soil, characterized by low $CaCO_3$ content and coarse texture, showed the highest N loss values from U, and the lowest values from UP treated soil. Laveen and Latene soils, similar in texture but different in $CaCO_3$ content, showed that N loss as NH_3 from Latene soil, which is higher in $CaCO_3$ content than Laveen soil, was greater than that from Laveen soil.

By reviewing the foregoing chapter, one can conclude that, generally higher N losses in the form of volatilized NH_3 resulted from U than UP treated soils, increasing N application rate, application of the N at the soil surface, coarse textured U treated soils, and soil with high $CaCO_3$ content. On the other hand, lower N losses in the form of

volatilized NH_3 resulted from UP than from U treated soils, reduced N application rate, UP or U mixed with the soil, coarse textured UP treated soils, and finer texture with low $CaCO_3$ content.

Measurements indicated that UP has the potential to reduce ammonia volatilization, under certain conditions. This is because UP reduces soil alkalinity due to its acidic nature. Volatilized NH_3 losses can be eliminated or reduced from the soil surface by acidity. Only under alkaline conditions can NH_3 exist (Jones, 1984). The effectiveness of acid incorporation with U in order to control N loss as volatilized NH_3 depends on the type and rate of the incorporated acid and the soil buffering capacity. By reacting with $CaCO_3$ and/or other alkaline materials, mineral acids will be neutralized rapidly leaving slightly acidic or neutral salts (Fenn and Richards, 1986).

When U is added to the soil it absorbs water, hydrolyzes to ammonium carbonate which is an unstable compound that decomposes to CO_2 and NH_4OH, and NH_3 is free to volatize into the atmosphere. The phosphoric acid (H_3PO_4) in UP retards U hydrolysis and decreases NH_3 volatilization due to delayed dissolution of U in soil (Bremner and Douglas, 1971; Stumpe et al., 1984).

An increase in volatilized NH_3 occurs with increasing NH_4-N forming fertilizer. This increase is dependent on the source of NH_4 and its effect on soil pH, which will affect the product of the source anion and soil Ca reaction. The solubility of this product will affect soil pH and N loss as volatilized NH_3 (Fenn and Kissel, 1973). Applying NH_4-N forming fertilizers to the soil surface results in retention of the NH_4^+ at the

exchange sites near the soil surface and less diffusion into the soil. This will allow more NH_3 exchange between the soil atmosphere, the air in soil pores, and the atmosphere, resulting in NH_3 volatilization.

Coarse textured soils have low retention and buffering capacity. Sandy soils can lead to leaching losses of acidity, whereas clay soils tend to conserve it. Therefore, adding acid sources to coarse textured soils will be more beneficial compared to little effect on fine textured soils, except at localized microsites (Jones, 1984). With high concentrations of hydrogen ions (H^+) buffering in the soil, the potential is reduced for NH_3 volatilization by allowing less of the ammoniacal N to become NH_3. The reduced NH_3 volatilization occurs because of the availability of the extra H^+ ions for the U hydrolysis step and the $HCO_3^- + H^+ \rightarrow H_2O + CO_2$ | reaction. A small increase in soil pH will result and less NH_4^+ will dissociate to $NH_3 + H^+$ (Ferguson et al., 1984). Fine textured soils have high CEC, more NH_4^+ will be retained by the soil in exchangeable form with less in the soil solution to equilibrate with NH_3. Because of the importance of NH_4^+ diffusion into the soil, the high CEC of the soil will restrict such diffusion from surface applications of ammonium compounds. Therefore, incorporating the fertilizers in the soil to a depth more than 5 cm will allow protection from volatilization. Urea phosphate seems to be more effective in reducing N losses in the form of volatilized NH_3 in coarse textured soil with all methods of application than finer textured soils. In highly calcareous soils, UP may not be very promising as

a means for reducing NH_3 volatilization, especially when applied to the surface.

It should be pointed out that the amounts of UP required to reduce NH_3 volatilization losses were very small. It is possible that a mechanism other than the localized reduction of soil pH may be involved. Perhaps UP is also acting as a urease inhibitor or in some way reduces the rate of hydrolysis of urea, thereby slowing the formation of NH_4^+ from urea.

Effect of Urea Phosphate on Leaching Soil Sodium and Salinity

The results of the study clearly demonstrate the beneficial effect of using acid containing fertilizers as amendments for the removal of soil Na and salinity. This effect was tested on two soils that differ in their physical and chemical characteristics. Pima loam and Crot clay were each treated with PHP, UP, MIX, SF, and Control at one and two times the equivalent of Na_{ex} in the soil. Soil columns were leached with tap water and leachate was analyzed for EC. Leaching was stopped when minimum change in leachate EC occurred. Each soil was dried, ground, sieved, and analyzed for certain chemical properties. Soil analysis indicated that acid containing treatments (PHP, UP and MIX) were effective in the removal of Na_{ex} and reducing soil salinity. Doubling the rate of application showed no effect on reducing or increasing most of the measured parameters. Generally, treatments were more effective (easier to reclaim) on Pima soil than Crot soil. This was because of the texture and Na_{ex} content as determining factors. All treatments were effective in reducing soil salinity measured as EC_e except for SF and Control in Crot soil. Soil

pH showed similar changes for both soils. Only SF and Control treatments were not effective. Acid containing fertilizers (as amendments) reduced Na_{ex} which was accompanied by an increase in Ca_{ex} and Mg_{ex}. These chemical changes occured because sulfuric and phosphoric acids in these fertilizers solubilized $CaCO_3$ in the soil. Calcium and/or Mg then replaces Na_{ex} on the exchange site of soil and soluble Na can then will be leached from soil solution.

It has been recognized for a long time that sulfuric acid (present in phosphoric solution) is a fast, effective material for the reclamation of sodic soils. However, corrosive and hazardous properties, has often restricted its use (Gregory, 1984). Urea phosphate, as an experimental fertilizer, showed the potential as an amendment for Na_{ex} removal. The effect of UP is based on the solubilization of Ca compounds. Sulfur waste material (SF) was not effective on most of the measured parameters, especially on Crot soil. However, mixing UP with SF showed a beneficial effect of enhancing the reclamation process. This enhancement of the reclamation process was obvious in Crot soil, which has a high pH value. This high pH may restrict the oxidation of elemental inorganic sulfur by soil microorganisms (Thiobacillus genus bacteria). Therefore, adding or mixing UP reduced soil pH and may have enhanced microbial activity of the soil.

As a general conclusion, UP is a fertilizer that will supply N and P as plant nutrients besides its additional capability, when compared to that of sulfuric acid, in reclaiming saline and alkali soils. Urea phosphate is easier to handle, transport, with less usage restrictions

than that of H_2SO_4. Perhaps smaller amounts than that used in the study could be also effective, since doubling the rate of applications from one to two equivalent of the amount of Na_{ex} showed no significant difference. In land reclamation projects, precise practical results must be obtained from field studies. Therefore, this greenhouse study should be followed up with simulated field studies or actual in situ field experiments using various fertilization rates.

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